Supplemental Report

SOURCES, ABUNDANCE, AND FATE OF GASEOUS ATMOSPHERIC POLLUTANTS SUPPLEMENT

Prepared for:

AMERICAN PETROLEUM INSTITUTE
1271 AVENUE OF THE AMERICAS
NEW YORK, N. Y. 10020

Attention: MR. W. A. BURHOUSE
ASSISTANT DIRECTOR

STANFORD RESEARCH INSTITUTE
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E R R A T A   S H E E T S

Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants

Project PR-6755, Supplemental Report

Replacements for Figure 14, page 62 *replaced*

and Figure 15, page 63 *replaced*

Page 68, lines 5 and 6 should read "...14.6 x 10^{12} g/yr NO_2-N."

Page 68, lines 8 and 9 should read "...Figure 15...501 x 10^8 tons/yr."

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June 1969

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SRI Project PR-6755

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PREFACE

As indicated by the title, this report is a supplement to our February 1968 report, "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants." For those having copies of the 1968 report, we wish to point out that the sections on carbon dioxide and carbon monoxide in this Supplemental Report are complete and can be substituted for similar sections in the earlier report. The supplemental data on nitrogen compounds are essentially the presentation of a new nitrogen cycle and the necessary supporting information. The information on sulfur compounds extends that included in the earlier report.

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I INTRODUCTION

In 1968 we published a comprehensive report, "Source, Abundance, and Fate of Gaseous Atmospheric Pollutants" (Robinson and Robbins, 1968),[*] that examined the present state of knowledge of the atmospheric cycles of a number of common gaseous air pollutants. In particular, this prior report covered in detail sulfur compounds, nitrogen compounds, organics, and carbon monoxide. A brief discussion of carbon dioxide was also presented. The pattern followed in the study included an analysis of emissions from the major natural and urban pollution sources, an estimation of the effectiveness of applicable atmospheric reaction processes, and a determination of the nature and effectiveness of the scavenging processes by which the material is finally removed from the atmosphere. The emissions and scavenging processes were considered on a global basis in contrast to a United States-only basis that is used in many discussions of air pollution. This earlier study was in a number of ways a new approach to considering air pollutants, especially in our integration of both natural and urban emissions as sources of the materials found in the atmosphere.

During the preparation of the previous analysis, there were several questions that, because of available time, were not covered in the detail that seemed desirable after the report was prepared. Thus, this supplemental analysis and report have been undertaken. This present report provides a more detailed analysis of the atmospheric buildup of CO_2, a newer analysis of the question of CO concentrations, another look at the atmospheric cycle of nitrogen compounds, and an analysis of the implications

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[*] Subsequently referred to as (I).

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of atmospheric trace chemistry differences in the northern and southern hemispheres.

We will point out in the present report, as we did in the previous one, that scavenging mechanisms exist in the natural environment for all of the gaseous pollutants that we are considering. These scavenging mechanisms have a direct bearing on the question of long term accumulations of pollutants in the atmosphere. However, these scavenging mechanisms do not operate fast enough to provide solutions for local urban air pollution situations. In fact, the existence of an air pollution situation is evidence that the available scavenging mechanisms have been overburdened by the local emission rates.

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II SUMMARY AND CONCLUSIONS

This reevaluation of natural and urban gaseous pollutants has added to the completeness of our previous report, especially in the case of CO_2 emissions.

For CO_2 emissions it is clear that atmospheric CO_2 concentrations are increasing at a rate of about 0.7 ppm per year and that the present concentration of about 320 ppm is about 10% higher than pre-1900 concentrations. The increase in atmospheric CO_2 represents about half the CO_2 produced by combustion sources since 1900. On the basis of current projections of fuel usage, CO_2 emissions in the year 2000 would be almost three times the estimated 1965 rate and would result in a 16% increase in atmospheric concentrations, to a level of 370 ppm.

Estimates of the impact that increased CO_2 might have on the global environment are difficult to make because of the complexity of the global atmospheric system. An increase in mean atmospheric temperature is possible because of the absorption of infrared radiation by CO_2, but the translation of this absorption into an atmospheric effect is difficult. The simple conclusion that an increase in absorbed radiation would provide more heat and melt the ice caps does not seem justified. It might be expected that the effect of additional CO_2 would be to cause some changes in the global atmospheric circulations, but what sort of changes and their results in terms of weather are not evident at this time.

The discussion of CO in the atmosphere has been revised extensively on the basis of newly available experimental data. One factor that seems clearly evident is that there is a natural source of CO in the ocean. The total contribution from this source is still unknown, but it could be a

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significant fraction of the pollutant emissions. No new data on possible
CO scavenging mechanisms are available and no cycle for CO has been pos-
tulated.

More detailed evaluations of SO_2 emissions were made. It is estimated
that 93% of the SO_3 pollutants are emitted in the northern hemisphere. On
a historical basis, SO_2 emissions doubled between about 1905 and 1940, and
again between 1940 and 1965. In the year 2000, SO_2 emissions are esti-
mated to be about 330 x 10^6 tons per year if significant changes do not
occur in the amount of emission control applied to SO_2 sources. On a
global basis, pollutant emissions of sulfur, as SO_2, may exceed the natural
sources of sulfur compounds about 1990.

We have also reevaluated the atmospheric nitrogen cycle. This new
evaluation includes allowances for some increases in the natural emissions
of NO and decreases in the deposition rates for NH_4 and NO_3 aerosols. The
result of these new calculations is a nitrogen cycle postulation in which
there is no need for an atmospheric reaction forming nitrate from NH_3 as
was required in the previous evaluation of the nitrogen cycle. No candi-
date reactions could be found for such a process. Thus the new estimate
seems to be a major step ahead.

On the basis of this supplemental study, some changes have been made
in our summary tabulation of atmospheric trace gas sources, concentrations,
and reactions. A revised summary tabulation is given in Table I.

A critical evaluation of this study of atmospheric trace gases would
doubtless point out that most conclusions are based on the barest minima
of data. This cannot be helped at this time because the necessary data
are not available. New information on atmospheric conditions is needed.

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Table 1

SUMMARY OF SOURCES, CONCENTRATIONS AND MAJOR REACTIONS OF ATMOSPHERIC TRACE GASES (June 1969)*

CONTAMINANT	MAJOR POLLUTION SOURCES	NATURAL SOURCES	ESTIMATED EMISSIONS		ATMOSPHERIC BACKGROUND CONCENTRATIONS	CALCULATED ATMOSPHERIC RESIDENCE TIME	REMOVAL REACTIONS AND SINKS	PRINCIPAL REFERENCES	REMARKS
			Pollution	Natural					
SO_2	Combustion of coal and oil	Volcanoes	146×10^6 tons	None	0.2 ppb	4 days	Oxidation to sulfate by ozone, or after absorption, by solid and liquid aerosols	Eriksson (1959, 1960, 1963) Junge (1963) Lodge and Pate (1966)	Photochemical oxidation with NO_2 and HC may be the process needed to give rapid transformation of $SO_2 \cdot SO_4$
H_2S	Chemical processes, sewage treatment	Volcanoes, biological action in swamp areas	3×10^6 tons	100×10^6 tons	0.2 ppb	2 days	Oxidation to SO_2	Junge (1963) Smith et al. (1961)	Only one set of background concentrations available
CO	Auto exhaust and other combustion	forest fires, terpene reactions, oceans (?)	271×10^6 tons	75×10^6 tons	0.1 ppm	<3 yr	None known, but large sink necessary	Bates and Witherspoon, Robinson, Robbins (1968, 1969)	Ocean contributions to natural source probably low
NO, NO_2	Combustion	Bacterial action in soil (?)	53×10^6 tons	NO 430×10^8 tons, NO_2 658×10^8 tons	NO 0.2 - 2 ppb, NO_2 0.5 - 4 ppb	5 days	Oxidation to nitrate after sorption by solid and liquid aerosols, hydrocarbon photochemical reactions	Junge (1963) Leighton (1961) Lodge and Pate (1966) Ripperton, et al. (1968)	Very little work done on natural processes
NH_3	Waste treatment	Biological decay	4×10^6 tons	1160×10^6 tons	6 ppb to 20 ppb	7 days	Reaction with SO_2, to form $(NH_4)_2SO_4$, oxidation to nitrate	Eriksson (1952) Georgii (1963) Junge (1963) Lodge and Pate (1966)	No quantitative rate data on oxidation of NH_3 to NO_3, which seems to be dominant process in atmosphere
N_2O	None	Biological action in soil	None	590×10^6 tons	0.25 ppm	4 yr	Photodissociation in stratosphere, biological action in soil	Bates and Hays (1967)	No information on proposed absorption of N_2O by vegetation
Hydrocarbons	Combustion, exhaust, chemical processes	Biological processes	88×10^6 tons	480×10^6 tons	CH_4 1.5 ppm, non CH_4 <1 ppb	16 yr (CH_4)	Photochemical reaction with NO/NO2, O2; large sink necessary for CH_4	Bates and Witherspoon (1952) Rhault (1967) Koyama (1963) Cavanagh et al. (1969)	"Reactive" hydrocarbon emissions from pollution = 27×10^6 tons
CO_2	Combustion	Biological decay, release from oceans	1.4×10^{10} tons	10^{12} tons	320 ppm	2-4 yr	Biological absorption and photosynthesis, absorption in oceans	Revelle (1965) Keeling Bolin and Eriksson (1959)	Atmospheric concentrations increasing by 0.7 ppm per year

* Reprinted with modifications from report of February 1968

III CARBON DIOXIDE IN THE ATMOSPHERE

A. Introduction

Air pollution analyses are typically concerned with compounds that are only present in the atmosphere in low concentrations and that pose well-recognized adverse reactions. This generality does not hold for the most commonly emitted pollutant, carbon dioxide. Carbon dioxide (CO_2) is an integral factor in the life cycle of the earth itself. At present, even though pollutant emissions of CO_2 are very great, the amount of CO_2 that is cycled through the biosphere is much greater, and there are several logical explanations as to why CO_2 is often neglected when pollutant emissions are tabulated.

As far as air pollution control is concerned, CO_2 is so common and such an integral part of all our activities that air pollution regulations typically state that CO_2 emissions are not to be considered as pollutants. This is perhaps fortunate for our present mode of living, centered as it is around carbon combustion. However, this seeming necessity, the CO_2 emission, is the only air pollutant, as we shall see, that has been shown to be of global importance as a factor that could change man's environment on the basis of a long period of scientific investigation. Because of this obvious relation, we believe that any discussion of atmospheric pollutants should also include a discussion of CO_2.

The possibility that changes in atmospheric CO_2 could change world climate is not a new idea. It was first proposed independently in America by Chamberlain in 1899 and in Sweden by S. Arrhenius in 1903. Since then CO_2 and possible geophysical effects have been the source of much discussion and investigation. At present, while we know a great deal more

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about the problem, we still cannot quantitatively evaluate the impact of
the accumulation of CO_2 in the atmosphere in terms of climatic change.
Considerable research is under way in a number of laboratories on this
problem, however.

As a basis for our discussion, the essential features of the CO_2 pol-
lution problem can be briefly outlined. First, CO_2 emissions are extremely
large and there has been for many years a gradual increase in atmospheric
CO_2 concentrations. Second, although there are sinks for CO_2 in both the
marine and biospheric environments, none of them is capable of counter-
balancing the increasing pollutant emissions. Third, the impact of CO_2
on the environment is through its interaction with the earth's radiation
balance. This is a very complex relationship, and the magnitude of pos-
sible environmental changes due to CO_2 are not now clearly defined.

B. Atmospheric Carbon Dioxide Emissions

. Carbon dioxide is present in the uncontaminated atmosphere at an
average concentration of about 320 ppm. The source is the oxidation of
carbonaceous materials in processes of respiration by both plants and
animals, decay of organic materials, and the combustion of organic fuels.
If there were no sinks for CO_2 it would obviously continue to increase;
however, at least until recently, there was a balance between the release
of CO_2 and the consumption of CO_2--by photosynthesis in plants, and by
the formation of calcium carbonate. This balance between environmental
sources and sinks has been disturbed by the emission to the atmosphere
of additional CO_2 from the increased combustion of carbonaceous fuels.

The amount of CO_2 emitted from pollution sources can be estimated
on the basis of the carbon content of the fuel. Table II is an estimate
of CO_2 emissions based on estimates of 1965 fuel usage. The total is
14.08×10^9 tons (12.8×10^{15} g). More than half the total CO_2 results

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Table II

ESTIMATED GLOBAL CO_2 EMISSIONS BASED ON 1965 FUEL USAGE

Fuel	Usage	CO_2 Factor	CO_2 Emission (tons)
Coal, lignite, etc.	$3,074 \times 10^6$ T	4,770 lb/T	7.33×10^9
Petroleum			
Gasoline	379×10^6 T		
Kerosene	100×10^6		
Fuel oil	287×10^6		
Residual oil	507×10^6		
	$1,273 \times 10^6$ T	6,320 lb/T	4.03×10^9
Natural gas	20.56×10^{12} ft^3	0.116 lb/ft^3	1.19×10^9
Waste incineration	500×10^6 T	1,830 lb/T	0.46×10^9
Wood fuel	466×10^6 T	2,930 lb/T	0.68×10^9
Forest fires	324×10^6 T	2,380 lb/T	0.39×10^9
Total			14.08×10^9 T (12.8×10^{15} g)

from coal and other solid fuels; petroleum combustion produces about 30%
of the total; and natural gas less than 10%. The remainder is due to mis-
cellaneous forms of combustion; forest fires, incineration of wastes, etc.

On the basis of the fact that the major commercial fossil fuels--coal,
petroleum, and gas--account for 89% of the estimated total, it is possible
to estimate the change in emission rates over the past 100 years. Figure 1
shows such an estimate based on decade averages for fuel consumption for
the period 1860-1960 (Revelle, 1965). These data are lower estimates of

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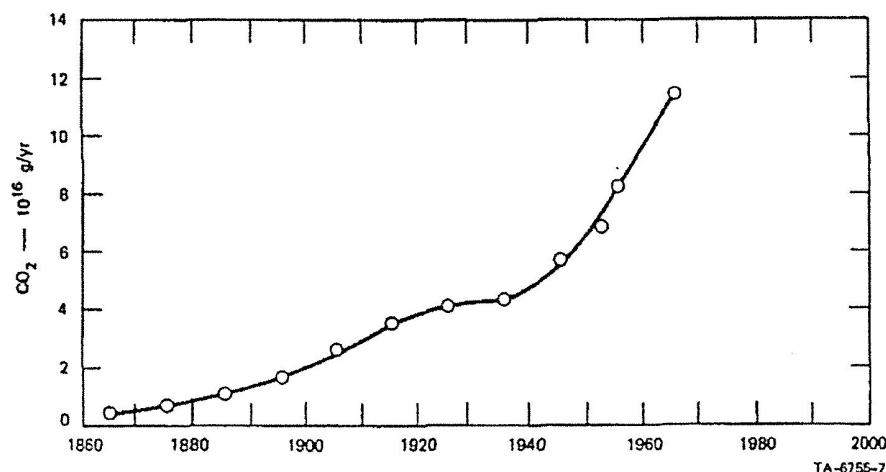
FIGURE 1   AVERAGE CO_2 EMISSIONS TO THE ATMOSPHERE FROM FOSSIL
FUEL COMBUSTION. Decade Average Data 1860-1960.

the CO_2 emissions because they do not take into consideration considerable
amounts of so-called noncommercial fuels--wood, wood waste, bagasse, etc.
In 1952 these fuels accounted for an estimated emission of 1.4×10^{15} g of
CO_2 (UN, 1956). In earlier years the per capita consumption of these fuels
was undoubtedly greater, but estimates of total usage are not available.
However, even if the 19th century data are low because of unaccounted for
fuel, there is still no doubt that there has been a significant increase
in the atmospheric emissions in the past 100 years. The increase has
probably been between 6 and 10 times.

Over the period covered by Figure 1 the total production of CO_2 from
fossil fuel combustion has amounted to 32.44×10^{16} g (Revelle, 1965).
This is equal to 13.5% of the total CO_2 in the atmosphere, which was
estimated from 1957 to 1959 data by Takahaski (1961) to be 2.41×10^{18} g.

C.   Atmospheric Carbon Dioxide Concentrations

As previously mentioned, the present estimate of the average CO_2 con-
centration in the atmosphere is 320 ppm. Fluctuations about this average
are quite large, depending on the nature of nearby sources and sinks. For

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example, during the growing season, concentrations decrease because plants use up CO_2 during photosynthesis.

One of the initial investigators of the possibility of CO_2 changes in the atmosphere was Callendar (1940). In 1958 he published an analysis of historical CO_2 measurements covering the period from 1870 to 1955 (Callendar, 1958). His results are shown in Figure 2 and indicate a 19th century CO_2 base concentration of about 290 ppm. This value is generally accepted as a reasonable approximation of the CO_2 concentration in the undisturbed atmosphere.
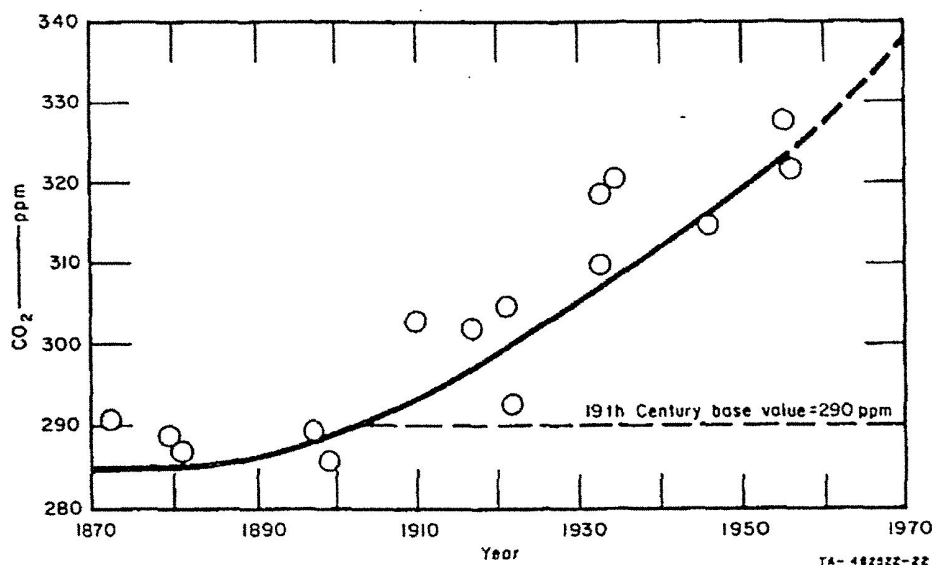
FIGURE 2   AVERAGE CO_2 CONCENTRA-
TION IN NORTH ATLANTIC
REGION, 1870–1956.
G. S. Callendar, Tellus 10, 243 (1958)

Figures 3 and 4 show CO_2 concentration data from Mauna Loa, Hawaii for the 6-year period 1958–1963 (Pales and Keeling, 1965). These data have been screened to eliminate local biasing, and the results should represent average conditions in the northern hemisphere over this time

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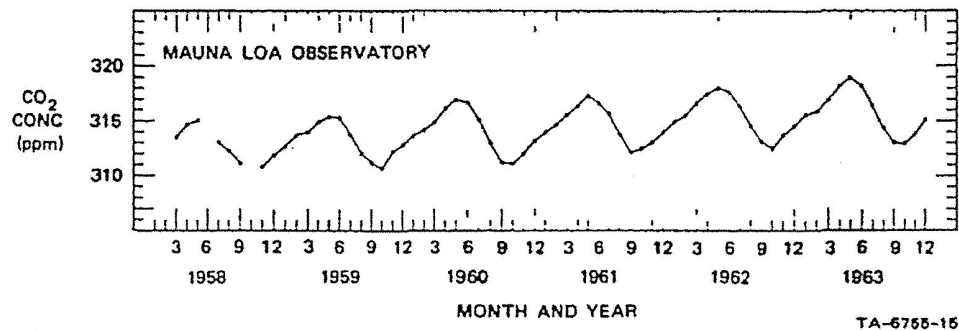
FIGURE 3 MONTHLY AVERAGE CONCENTRATION OF ATMOSPHERIC CO_2
AT MAUNA LOA OBSERVATORY VERSUS TIME. Pales, J. C.,
and C. D. Keeling, J. Geophys. Res. *70*, 6066, 1965.
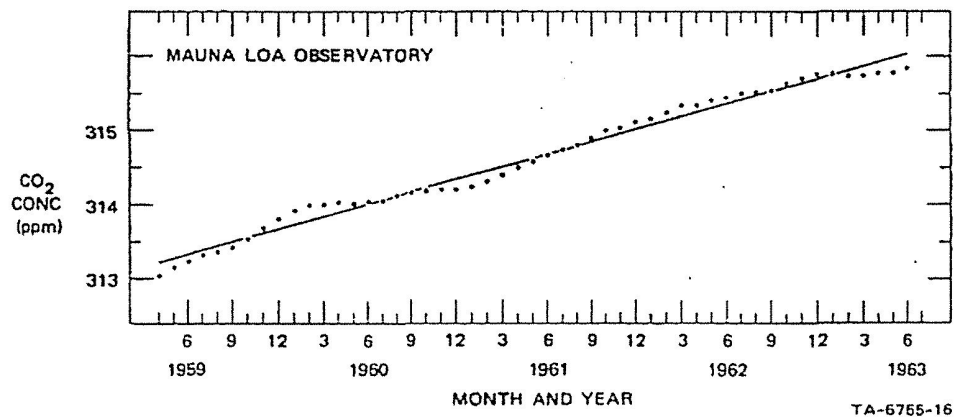
FIGURE 4 TWELVE-MONTH RUNNING MEAN OF THE CONCENTRATION
OF ATMOSPHERIC CO_2 AT MAUNA LOA OBSERVATORY.
Means are plotted versus the sixth month of the appropriate 12-month
interval. The straight line indicates a rate of increase of 0 68 ppm/yr.
(Pales, J. C, and C. D. Keeling, J. Geophys. Res. *70*, 6066, 1965)

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period. Figure 3 shows clearly the annual cycle of CO_2 concentrations, with maximum concentrations occurring in the late spring and minimums in the fall. A gradual trend toward rising concentrations is identifiable in Figure 3, but Figure 4, which is a plot of the 12-month running mean concentration, shows the upward trend much more clearly. As shown by Figure 4, the CO_2 concentration has increased from about 313.3 ppm for the 12 months before June 1959 to a concentration of 315.9 ppm for the 12 months before June 1963. The straight line fitted to the data of Figure 4 indicates an annual rate of increase of 0.68 ppm.

There is an apparent difference of several ppm between these Hawaiian data and the 1955 results reported by Callendar in Figure 2. This difference is probably due to various local effects resulting from land-based sampling in the case of Callendar's data. The Hawaiian data and other similar observations from locations where good exposure to the free atmosphere is attainable probably most nearly represent the present state of the well-mixed troposphere.

The rate of increase shown by the Mauna Loa data seems to be characteristic of global CO_2 concentrations. Bischof and Bolin (1966) show that Scandinavian data fit the postulated 0.7-ppm/yr rate obtained from the Mauna Loa data. Figure 5 shows average monthly data from the Antarctic for the period September 1957-November 1959 (Keeling, 1960). The rate of increase here is about 1 ppm/yr, which, considering the limited span of the data, seems to be comparable to the northern hemisphere data. The average 1959 Little America concentration of about 314 ppm is also comparable to the Mauna Loa average of 313.3 ppm indicated by Figure 4.

Around 1960, CO_2 concentrations were increasing by 0.7 ppm or 0.22% of a 315-ppm average concentration, and in this same period emissions from fossil fuel, as shown in Figure 1, were adding about 10^{16} g of CO_2 per year

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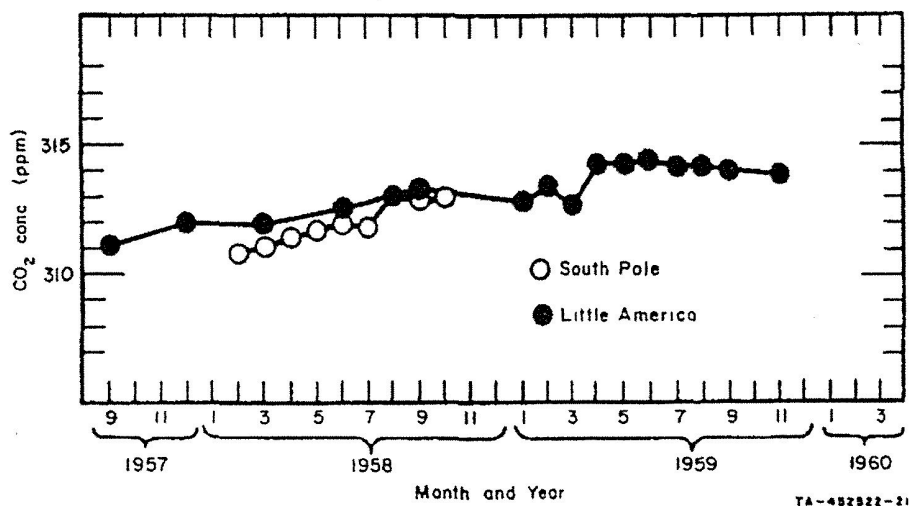
FIGURE 5   VARIATIONS IN CO_2 CONCENTRATIONS IN THE ANTARCTIC
C. D. Keeling, Tellus, *12*, 200, 1960

to the atmosphere for a 0.42% rate of addition. Thus, it appears that
very nearly half the CO_2 emitted to the atmosphere remains there. Revelle
(1965) came to a similar conclusion.

The data on atmospheric CO_2 are quite voluminous and it is not pos-
sible to present them in detail in this discussion. However, the data
indicate that any differences between the hemispheres are small and that
there has been a readily detectable increase of CO_2 in the atmosphere.
This increase was originally postulated on the basis of an analysis of
19th century measurements. The increase from a 19th century base of
290 ppm to a late-1960 average of about 320 ppm is 10%.

D.   Scavenging Mechanisms for Atmospheric Carbon Dioxide

The previous discussion has mentioned that processes in the biosphere
and the oceans act to maintain an equilibrium situation between the atmos-
phere, the biosphere, and the oceans.

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In the biosphere, photosynthesis removes CO_2 from the atmosphere and forms plant carbon. The ultimate fate of most of this carbon is deposition as litter and humus followed by decay and the rerelease of CO_2 to the atmosphere. Thus, the cycle is completed.

Detailed studies of the relationship between atmospheric CO_2 and the biosphere have been made. Lieth (1963) pointed out that the exchange between the atmosphere and the biosphere is very intensive through the two processes of assimilation and respiration. The total amount of carbon uptake by land plants has been estimated for 10° latitude belts by Junge and Czeplak (1968) using data developed by Lieth (1965). These data, in terms of a global distribution of CO_2 uptake, are given in Table III. The total annual rate of CO_2 vegetation uptake is 141×10^{15} g, with 83×10^{15} g or 59% occurring in the northern hemisphere. If vegetation uptake were the only scavenging mechanism for the 2.41×10^{18} g of CO_2 in the atmosphere, the residence or turnover time for CO_2 would be 17 years. This estimate is based on the estimate of the total vegetation production capacity of the world shown in Table III. In many references the CO_2 residence time resulting from vegetation scavenging is often given as being about 30 years and this represents understandable variations in estimates of the total production of the biosphere.

Table III

TOTAL CO_2 UPTAKE BY LAND PLANTS*
(10^{15} grams/year)

Latitude($^{\circ}$)	0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-90
Northern hemisphere	23.5	14.3	11.7	9.2	10.3	9.2	4.8	0
Southern hemisphere	26.4	18.0	8.8	4.0	0.7	0	0	0

* References: Junge and Czeplak (1968); Lieth (1965).

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It is obvious that there is considerable variation in CO_2 production and uptake rates within various vegetation communities. For example, Lieth (1963) estimates that a tropical forest in Malaya has an annual productivity equivalent to 37.5 metric tons of CO_2, and that this is equivalent to a turnover time for the CO_2 above this tropical forest of 0.8 years. A similar estimate for a forest in Europe resulted in an annual productivity rate equivalent to 15 metric tons of CO_2 and a CO_2 turnover time of two years.

Although the biosphere is important in the CO_2 cycle, the role of the ocean in the CO_2 cycle has long been recognized as the dominant one, and various estimates of the average atmospheric residence time for CO_2 relative to the uptake rate of the oceans have been calculated. Some of the more detailed calculations have been made by Young and Fairhall (1968) using data on bomb-produced C^{14}. If only the troposphere is considered, their estimate is that the CO_2 uptake rate of the ocean is sufficient to give a mean residence time of CO_2 in the atmosphere of 2.5 years. This average value is made up of two residence times, 3.9 years for the northern hemisphere and 1.9 years for the southern hemisphere.

This mean tropospheric residence time of 2.5 years and the tropospheric CO_2 mass of 202×10^{16} g, 84% of the atmospheric total, indicates a global oceanic uptake rate of 81×10^{16} g/year. If this is the only sink for the CO_2 in the stratosphere as well as the troposphere, an average atmospheric CO_2 residence time of three years is indicated. Other calculations for the CO_2 atmospheric residence time have varied from less than two years to about 20 years (Young and Fairhall, 1968).

Within the ocean, CO_2 is consumed in the growth of marine plants and animals just as it is in the biosphere. The production of CO_2 during the decay of this material is a major source of both atmospheric and marine

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CO_2. The CO_2 that is used by marine organisms is primarily used to build the organic mass of the organism, but part of the CO_2 is used to generate shells and other calcareous material.

Biological activity including CO_2 takes place for the most part in the upper 50 to 100 m of the ocean. This is the mixed layer. However, obviously as these organisms die there is considerable settling of material out of the mixed layer and into the deep water layer. This settling action is a major sink for carbon and thus for atmospheric CO_2 because the deep water is essentially isolated from the atmosphere. The mixing time for the deep water has been estimated to be upwards of 500 years.

In the late 1950s there was considerable new scientific discussion about the secular increase of CO_2, as a result of published studies of atmospheric levels by a number of researchers, including Revelle and Suess (1957) and Callendar (1958), and predictions of resulting temperature changes in the atmosphere by Kaplan (1960), Plass (1959), and others. Initially in these discussions Callendar's (1949, 1958) estimate of about a 10% secular rise since 1900 in atmospheric CO_2 was discounted (see e.g., Revelle and Suess, 1957; or Slocum, 1955) primarily on the assumption that there would be relatively rapid exchange of CO_2 between the oceans and the atmosphere. Since CO_2 is highly soluble, one argument was that because the oceans are a reservoir of CO_2 that is very large compared with the atmosphere--about 60 times as much CO_2 is stored in the oceans as in the atmosphere--equilibrium between the ocean and the atmosphere would be achieved rapidly enough to minimize any significant atmospheric CO_2 accumulation due to combustion emissions. Initial data on C^{12}/C^{14} relationships in the atmosphere and the oceans, the so-called "Suess effect," also indicated that combustion-derived CO_2 was not very significant in any change in atmospheric CO_2 levels (Revelle and Suess, 1957).

More information became available in the late 1950s, however, and the subsequent detailed analysis of the atmosphere-ocean system showed several important things relative to CO_2 buildup. First, IGY sampling data showed that Callendar's postulated increase of CO_2 was occurring and at a rate of about 0.7 ppm/year, as we have mentioned. Second, careful analysis of the ocean/atmosphere exchange processes indicated that only the relatively shallow mixed layer was important and that this layer provided very little in the way of storage to moderate any secular increase of atmospheric CO_2.

Bolin and Eriksson (1959) show that this low storage factor is due to a buffering mechanism set up in the sea by dissolved CO_2. It is related to the dissociation equilibrium between CO_2 and H_2CO_3 on the one hand and HCO_3 and CO_3 ions on the other. The net result is that a 10% change in atmospheric CO_2, such as from 290 to 320 ppm, would be balanced by only a 1% increase in the CO_2 content of sea water. This buffering mechanism was originally pointed out by Revelle and Suess (1957), but it was unimportant in their analysis because in their ocean model it was applied to the whole volume of the ocean. Bolin and Eriksson (1959), using the more realistic two-layer model of the ocean, showed that when this buffering mechanism, acting in the mixed surface layer, was taken in account, there was good agreement between the observed and postulated CO_2 changes in the atmosphere due to fossil fuel combustion. They also showed that when changes in dissociation equilibrium resulting from CO_2 transfer were accounted for, C^{12}/C^{14} ratios in the atmosphere and the oceans were in agreement with an increase in atmospheric CO_2 of about 10%.

Various authors have from time to time attempted to relate atmospheric CO_2 changes to various changes in the physical properties of the oceans or to changes in the biosphere. Eriksson (1963) made a comprehensive analysis of the possible changes in CO_2 that might result from

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changes in oceanic conditions. His conclusion was that if the temperature of the oceans increases by $1^{\circ}C$, the atmospheric CO_2 increases by about 6%. If only the mixed layer of the ocean is considered, data given by Junge and Czeplak (1968) permit calculation of the effect of a limited temperature change of surface water. The result is that if the mixed layer alone increased in temperature by $1^{\circ}C$, the atmospheric CO_2 would increase by about 0.4%. We conclude with regard to recent increases in atmospheric CO_2 that any reasonable changes in oceanic temperatures could only result in local fluctuations in atmospheric CO_2 and not in any changes of global importance.

Other changes such as water volume, seawater chemistry, and variations in the marine biomass may also be discounted as contributors to short term changes in atmospheric CO_2 levels; although these factors may be significant factors in climatic changes over a geologic time scale (Eriksson, 1963).

Changes in the biosphere are also sometimes linked to changes in atmospheric CO_2. It is pointed out that vegetation responds with increased production under increased concentrations of CO_2 and that an increase in the mass of the biosphere could be a moderating influence on any increase in atmospheric CO_2. A rapid increase in the production rate of the biosphere could also cause an increase in atmospheric CO_2, at least until a new stable position was established. Data on the mass of material in the biosphere is relatively crude; however, it seems unlikely that the observed rise in atmospheric CO_2 has been due to changes in the biosphere.

E.   Effects of Atmospheric Carbon Dioxide Concentrations

Our discussion has already indicated that atmospheric CO_2 concentra-
tions are of concern because of the effect of atmospheric CO_2 on the radi-
ation balance of the earth. The effect of CO_2 is a result of the inter-
ception of long-wave radiation from the earth's surface and its reradiation
to the surface. Under the simplest set of assumptions for this situation
the earth's surface reaches equilibrium at a higher temperature, and this
is recorded as an increase in air temperature.

Under more realistic conditions, it is recognized that this situation
is not a simple relationship. One of the major factors is an interaction
between the CO_2 and water vapor in the atmosphere. Water vapor is signi-
ficant because it also absorbs strongly in the infrared. Cloudiness, be-
cause it intercepts incoming radiation, is also an important parameter.
However, the most important interaction is between the radiation regime
and the general atmospheric circulation, since it is the circulation pat-
tern that determines the weather.

One of the most detailed analyses of the temperature effect from CO_2
changes has been carried out by Manabe and Wetherald (1967). This model
is based on an atmosphere that is in radiative convective equilibrium,
and the model approaches the real situation by estimating temperature
effects for the atmosphere itself instead of for the earth's surface as
had prior models. In addition, previous models such as that used by
Möller (1963) had usually been especially sensitive to some specific
sets of conditions and produced very different end results with rela-
tively minor changes in some critical assumptions. Manabe and Wetherald
claim that this does not occur in their model, and thus they argue that
they have probably come closer to approximating the real situation than
have previous writers.

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A number of different sets of conditions were used by Manabe and Wetherald (1967), but probably their most representative model is one in which relative humidity is maintained constant and an average amount of cloudiness is included. The result is that for a change in CO_2 from 300 to 600 ppm, an increase in temperature of $2.36^\circ C$ is estimated. For a CO_2 decrease from 300 to 150 ppm, a temperature decrease of $2.28^\circ C$ is predicted. These data indicate that an increase to 330 ppm would produce an estimated temperature increase of about $0.3^\circ C$. In summarizing their CO_2 modeling experiments, Manabe and Wetherald (1967) point out the following specific factors:

1. The higher the CO_2 concentration, the warmer is the equilibrium temperature of the earth's surface and the troposphere.

2. The higher the CO_2 concentration the colder is the equilibrium temperature of the stratosphere.

3. Relatively speaking, the stratosphere responds much more strongly to a change in CO_2 content than does the troposphere.

The importance of these CO_2 model calculations is that we expect that the CO_2 concentration in the atmosphere will continue to increase as our combustion economy continues to consume increasing amounts of fossil fuel. Various estimates have been made about the possible CO_2 that might be released to the atmosphere. Table IV is an estimate of CO_2 emissions for the period to the year 2000. The base point for this information is our estimate for 1965 in Table II and estimates of global changes in fuel use. The estimated increases for coal (0.2%/yr), petroleum (6.2%/yr), and natural gas (7.2%/yr) are based on recent estimates of growth to 1980, extrapolated to 2000 (SRI, 1969). For the minor sources, the change in incineration is intermediate between the major fuels, and no changes are estimated for the burning of fuel wood or for forest fires. On a relative basis, CO_2 emissions in the year 2000 are almost three times higher than those in 1965. The estimated total CO_2 emission over the period 1965-2000 is

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Table IV

PROJECTED CO_2 EMISSIONS: 1965-2000

| | 1966 | | | Emissions, 10^9 T | | | |
	Usage	CO_2 Factor	1965	1970	1980	1990	2000
Coal	$3,074 \times 10^6$ T	4,770 lb/T	7.33	7.40	7.55	7.70	7.85
Increase	0.2%/yr						
Petroleum	$1,273 \times 10^6$ T	6,320 lb/T	4.03	5.28	8.57	13.90	22.50
Increase	6.2%/yr						
Natural gas	20.56×10^{12} ft^3	0.116 lb/ft^3	1.19	1.62	2.79	4.80	8.27
Increase	7.2%/yr						
Incineration	500×10^6 T	1,830 lb/T	0.46	0.51	0.61	0.73	0.88
Increase	2%/yr						
Wood fuel	466×10^6 T	2,930 lb/T	0.68	0.68	0.68	0.68	0.68
No change							
Forest fires	324×10^6 T	2,380 lb/T	0.39	0.39	0.39	0.39	0.39
No change							
Total			14.08	15.88	20.59	28.20	40.57
Relative change			100%	113%	146%	200%	288%

845×10^9 tons or 770×10^{15} g. If half the emitted amount remains in the atmosphere, as we previously calculated, the total CO_2 in the atmosphere would be about 2.8×10^{18} g or about a 16% increase from 320 ppm in 1960 to about 370 ppm in 2000. On the basis of Manabe and Wetherald's (1967) calculations, a 50-ppm increase would be translated into an average atmospheric temperature increase of $0.5^{\circ}C$.

Revelle (1965) points out that total recoverable fossil fuels as of 1965 are estimated to be about 10^{12} tons, with a CO_2 equivalent of 7.9×10^{18} g or 330% of the 1960 atmospheric CO2. If, as indicated by the 1958-63 data, half of this stays in the atmosphere, then ultimately

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the atmospheric CO_2 concentration could increase from 320 ppm to about 850 ppm, as recoverable fossil fuels are used up.

Most generalized analyses of the CO_2 situation infer that a given increase in atmospheric temperature could cause a gradual melting of the polar ice caps. Revelle (1965), for example, states that if half the energy associated with a 2% increase in radiation energy, as might occur from a 25% increase in CO_2, were available to melt the polar ice caps, the ice would disappear in about 400 years. Melting ice caps, if they occurred, would obviously result in inundation of coastal areas. However, when the details of the total atmospheric system are considered, it is not at all obvious what the result of added CO_2 might be.

Fletcher (1969) is carrying out a long term detailed study of the relationship between the Antarctic ice cap and world climate. Fletcher's research consists of developing models of ocean/atmosphere heat exchange and relationships to global circulation patterns. Observing ice conditions in the Antarctic, he has found apparent global climatic relationships. Increases in ice area in the Antarctic were found to correspond to an intensification of the zonal circulation in the southern hemisphere and, to a lesser extent in the northern hemisphere, accompanied by a warming trend over most of the northern high latitudes. Conversely, decreasing ice in the Antarctic, such as has been postulated as resulting from an increase in atmospheric CO_2, corresponds to a weakening of the zonal circulation in both hemispheres, an increased prevalence of meridianal circulation patterns in the northern hemisphere, and a cooling over most of the northern latitudes (Fletcher, 1969).

These correlations by Fletcher are based on what has occurred in the past, and with our present knowledge we are not justified in predicting future effects of CO_2 on the basis of these correlations. There are too many complicating factors in the total ocean/atmosphere system to permit

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solution at this time. For example, Möller (1963) points out that a fairly significant 10% increase in CO_2 can be counterbalanced by a 3% change in atmospheric water vapor or a 1% change in total average cloudiness. It is doubtful that we are equipped at present to detect changes of this magnitude in either water vapor or cloudiness.

Although, as we mentioned before, there are other possible sources for the additional CO_2 now being observed in the atmosphere, none seems to fit the presently observed situation as well as the fossil fuel emanation theory does.

F.   Summary of Carbon Dioxide in the Atmosphere

Revelle and others have made the point that man is now engaged in a vast geophysical experiment with his environment, the earth. On the basis of our present knowledge, significant temperature changes could be expected to occur by the year 2000 as a result of increased CO_2 in the atmosphere. These could bring about long term climatic changes.

More recently, McCormick and Ludwig (1966) have provided an analysis of the possible worldwide change of atmospheric fine particles. An increase in fine particulate material may have the effect of increasing the reflectivity of the earth's atmosphere and to reduce the amount of radiation received from the sun. Thus this effect would be the opposite of that caused by an increase in CO_2. The argument has been made that the large scale cooling trend observed in the northern hemisphere since about 1955 is due to the disturbance of the radiation balance by fine particles and that this effect has already reversed any warming trend due to CO_2.

Any secular changes due to increases in pollutant aerosols would be limited almost exclusively to the northern hemisphere. This would result from the relatively small amount of pollution in the southern hemisphere

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and the slow or negligible transfer of aerosols across the equator. The CO_2 cycle is such that concentrations in the two hemispheres are equal.

It is rather obvious that we are unsure as to what our long lived pollutants are doing to our environment; however, there seems to be no doubt that the potential damage to our environment could be severe. Whether one chooses the CO_2 warming theory as described by Revelle and others, or the newer cooling theory indicated by McCormick and Ludwig, the prospect for the future must be of serious concern.

It seems ironic that, in air pollution technology, we are so seriously concerned with small scale events, such as the photochemical reactions of trace concentrations of hydrocarbons and the effect on vegetation of a fraction of a part per million of SO_2, whereas the abundant pollutants-- CO_2 and submicron particles--which we generally ignore because they have little local effect, may be the cause of serious worldwide environmental changes.

IV ATMOSPHERIC CARBON MONOXIDE

A. Introduction

Carbon monoxide has been considered an important atmospheric pollutant for many years because of its prevalence in automobile exhaust and in the effluents from poor combustion. In spite of widespread knowledge about the toxicity of CO, there have been many fatalities resulting from exposure to excessive CO. Because of the hazards it posed, initial air pollution studies of CO in urban atmospheres were carried out mostly to determine whether specific segments of the urban population, e.g., traffic police and tunnel toll takers, were exposed to toxic levels of CO. However, in more recent urban atmospheric studies, such as the USPHS Continuous Air Monitoring Program, CO measurements have been included as an indication of urban air quality.

It has typically been assumed that the only sources of CO were combustion sources, and that CO presented a relatively simple pollutant situation. However, as we will describe later, some natural sources of CO seem to be clearly indicated. This is a new dimension in CO studies, and there are a number of new problems that must be included. Of major importance is the nature of the scavenging mechanisms for CO. We will discuss various possibilities in some detail, but at present no really satisfactory sink or sinks can be described.

B. Atmospheric Carbon Monoxide Concentrations

The presence of CO in urban atmospheres at concentrations as high as 50 to 100 ppm has been recognized for many years, but it was not discovered that CO was present in trace amounts in the ambient atmosphere until Migeotte (1949) detected absorption lines in the solar spectrum around 4.7μ. Later, Migeotte and Neven (1950) confirmed the identification with measurements

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in Switzerland, and further spectra were also obtained by Shaw, et al. (1951). Some confusion arose when Adel (1949), using spectra obtained at Flagstaff, Arizona was unable to detect the CO lines found by Migeotte in his Ohio spectra. However, when further studies in United States and Europe continued to show the CO lines in the solar spectra, it became generally assumed that CO was a more or less permanent but perhaps highly variable atmospheric constituent. On the basis of the solar spectra from the early 1950s an average ambient CO concentration of 0.2 ppm was estimated (Junge, 1963).

In 1966, Robbins, Borg, and Robinson (1968) built a new instrument for CO detection that was sufficiently sensitive to measure ambient concentrations down to at least 0.005 ppm. The paper also included some ambient CO data from remote locations. These early data are shown in Table V.*

In the summer and fall of 1967 three studies of CO were made using this CO recorder in the field in contrast to the flask sampling data shown in Table I. The first of these field studies consisted of approximately three weeks of daily sampling on the Greenland ice cap, 400 miles east-northeast of Thule at Inge Lehmann Station; 78 N, 39 W (Robinson and Robbins, 1969a). This sampling was carried out in late July and early August 1967. The results of this sampling are shown in Figure 6, and indicate an average CO concentration of about 0.11 ppm with a low concentration of about 0.09 ppm and a high value of over 0.5 ppm. This latter very high data occurred midway through the test period, around July 29, 1967. Subsequent analysis of air mass trajectories showed that this high concentration period coincided with the passage of an air mass that had previously passed south of the Great Lakes. It was

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* Reprinted from (I).

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Table V

TYPICAL ATMOSPHERIC CARBON MONOXIDE CONCENTRATIONS
FOUND IN NONURBAN AREAS

Place	Date	Local Time	Wind Direction and Velocity (mph)	CO Concentration (ppm)
Camp Century, Greenland	7/3/65	1245	SE-8	0.90
Camp Century, Greenland	7/3/65	1245	SE-8	0.85
Camp Century, Greenland	7/5/65	0800	SE-15	0.24
Camp Century, Greenland	7/5/65	0805	SE-15	0.32
North Coast, California	6/23/65	1400	W-8	0.85
North Coast, California	6/24/65	1400	W-10	0.80
Coastal Forest, California	6/24/65	1130	Calm	0.80
Crater Lake, Oregon (7000 ft elev)	9/27/65	0905	NE-22	0.30
Crater Lake, Oregon	9/28/65	0835	Lt. & Var.	0.08
Crater Lake, Oregon	9/28/65	1650	W-4	0.06
Crater Lake, Oregon	9/29/65	0910	Lt. & Var.	0.03
Crater Lake, Oregon	9/29/65	1700	Lt. & Var.	0.05
Patrick Point, Calif., Coast	10/02/65	1630	S-5	0.04
Patrick Point, Calif., Coast	10/03/65	1800	W-10	0.04
Patrick Point, Calif., Coast	10/04/65	1145	W-10	0.04
Patrick Point, Calif., Coast	10/05/65	0840	E-2	0.80
Patrick Point, Calif., Coast	10/05/65	1320	W-5	0.06
Patrick Point, Calif., Coast	10/06/65	1320	Lt. & Var.	0.34
Patrick Point, Calif., Coast	10/06/65	1650	W-8	0.06
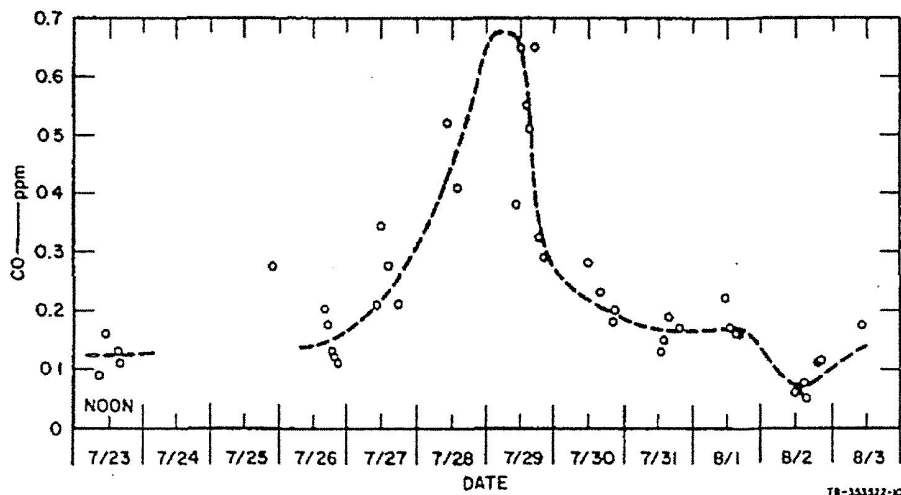
FIGURE 6   ATMOSPHERIC CARBON MONOXIDE CONCEN-
TRATIONS, JULY 23—AUGUST 3, 1967 INGE
LEHMANN STATION, GREENLAND—78° N, 39° W

concluded that the high CO concentrations resulted from CO emissions in the northeastern part of the United States.

Shortly after this Greenland program, about three weeks of CO field data were recorded at Point Barrow, Alaska, 71 N, 157 W. At this station, CO concentrations were generally below 0.10 ppm with an average of about 0.09 ppm (Cavanagh, et al., 1969). During the period of sampling there were no large deviations from this average, such as were seen in Greenland.

Since January 1967, CO concentrations have been measured on five voyages in different parts of the Pacific. These CO sampling expeditions included Cruises 27, 29, and 31 of the USNS Eltanin and Cruises 41 A-B and 41 H of USNS Perseus.

On Cruise 27, a series of flask samples taken approximately along 170°E between 65° and 77°S (Robinson and Robbins, 1968). The results, as indicated in Figure 7, showed that CO increased southward from about 0.03 ppm at 65°S to 0.08 ppm at 77°S. On January 13-14 a series of four

30
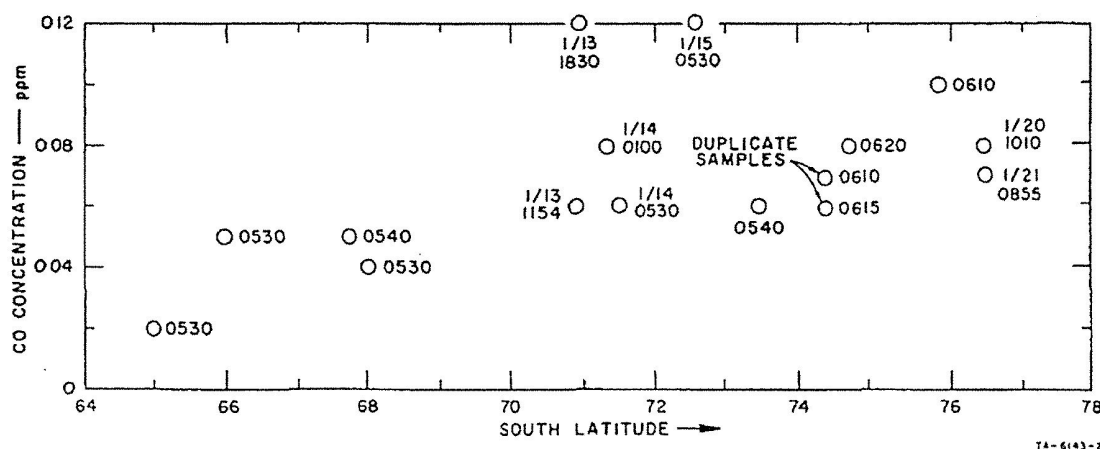
FIGURE 7   CARBON MONOXIDE CONCENTRATIONS, ELTANIN CRUISE 27 BETWEEN 168°
AND 177° E LONGITUDE, JANUARY 1967

samples at 1154, 1830, 0100, and 0530 local time showed a strong diurnal
cycle, with a high evening concentration of 0.12 ppm compared with 0.06 ppm
at 1154 and 0530. Similar diurnal variations have been observed in sub-
sequent samplings.

Flask samples were also taken on the Eltanin Cruise 29 westward along
28°S between Chile and Australia (Robinson and Robbins, 1968). The results
shown in Figure 8 indicate a much more irregular pattern than on Cruise 27
and the concentrations are generally higher. It appears that in the east-
ern Pacific, near Chile, the concentrations are around 0.05 ppm and in-
crease to perhaps 0.10 ppm between 130° and 150°W. Farther west concentra-
tions decrease again.

Cruise 31 of USNS Eltanin was a direct voyage from San Francisco to
New Zealand in November and December, 1967. On this trip CO concentrations
were measured (Robinson and Robbins, 1969b), using the new continuous CO
analyzer.

The CO concentration at approximately local noon is shown in Figure 9
on a scale that is approximately proportional to distance on a straight
line course from San Francisco to New Zealand. The only major deviation

31
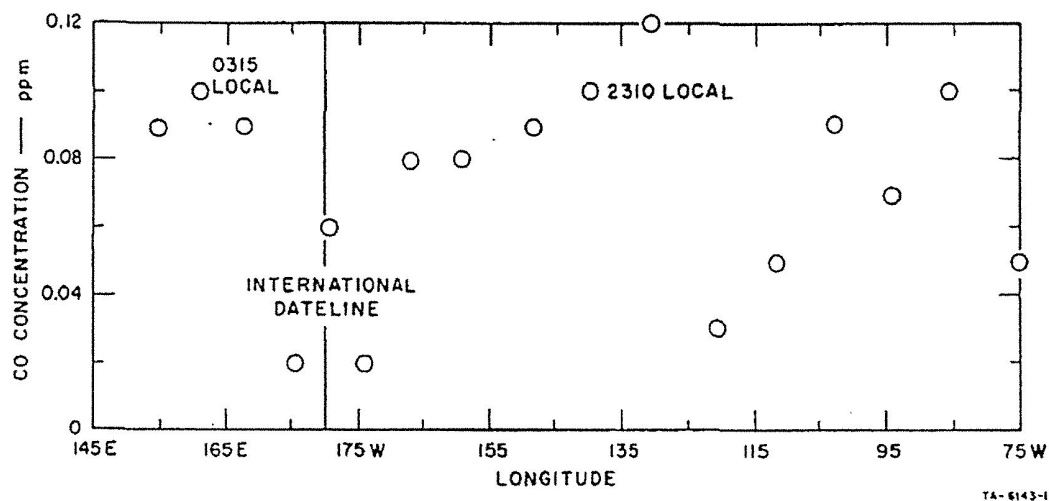
FIGURE 8   CARBON MONOXIDE CONCENTRATIONS, ELTANIN CRUISE 29 ALONG 28°S
LATITUDE, JUNE—JULY 1967
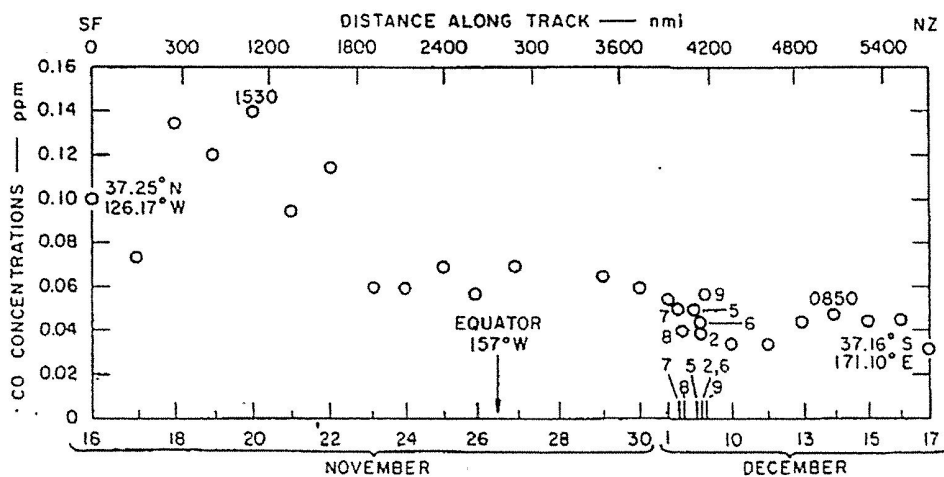
FIGURE 9   CO CONCENTRATIONS AT LOCAL NOON ELTANIN CRUISE 31,
SAN FRANCISCO TO NEW ZEALAND, NOVEMBER—DECEMBER 1967

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from this straight course was in early December around Pago Pago when a more irregular pattern was sailed. The general pattern shows increased CO concentrations from around 0.09 ppm near California to as high as 0.14 ppm east of Hawaii at 23°N, 140°W on November 20. From this point the decrease is relatively rapid to 0.06 ppm on November 23 at a latitude of 12°N, 149°W. Concentrations remained at about 0.06 to 0.07 ppm until about December 1 at latitude 13°S, 172°W. Between December 1 and 10 there were variations between 0.04 and 0.06 ppm. After December 10 at 19°S, 176°W the average concentration was 0.04 ppm. Cruise 31 crossed the track of Cruise 29 on December 14 at 28°S, 176°E. The recorded noon CO concentration of 0.048 ppm is higher than the 0.020-ppm sample obtained in this general area on the earlier cruise, but both samples indicate relatively low concentrations.

In June 1968 an east-west Pacific crossing was made on the USNS Perseus, Cruise 41 AB in which the CO recorder was again used to provide continuous data. The return voyage of the Perseus, Cruise 41 H, was made in late July and early August, 1968. The average daily CO concentrations observed on these two trips are shown in Figure 10 (Robinson and Robbins, 1969b). There does not seem to be any clear trend in these data, or at
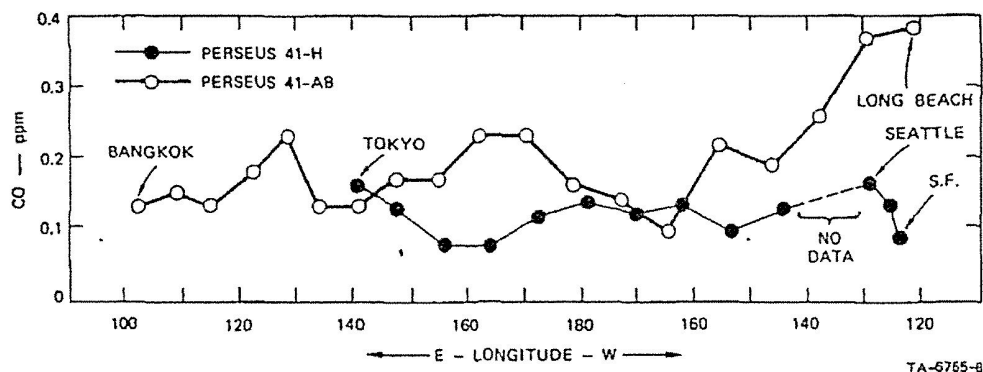
FIGURE 10   AVERAGE DAILY CO CONCENTRATIONS AS A FUNCTION OF LONGITUDE ACROSS THE NORTH PACIFIC, USNS PERSEUS TRIPS 41 A, B, H, JUNE–JULY, 1968

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least nothing comparable with that shown for the north-south data in
Figure 9.

About the only trend shown is that the data taken in July and August
were higher than the June data. The average daily concentration for the
westbound trip in June is 0.12 ppm, and for the mid-summer return trip
the daily average was 0.18 ppm. In the mid-Pacific generally east of
the dateline, the east- and west-bound tracks of the Perseus coincided.

All of these Pacific data have been combined to provide an indica-
tion of an average north-south CO concentration pattern over the Pacific.
This is shown in Figure 11 (Robinson and Robbins, 1969b). Average daily
concentrations or individual flask samples have been grouped into 5° lati-
tude classes. The individual values are shown. The curve was fitted by
eye and is an attempt to indicate an average north-south CO profile. On
the basis of this curve, Arctic concentrations are about 0.1 ppm. The
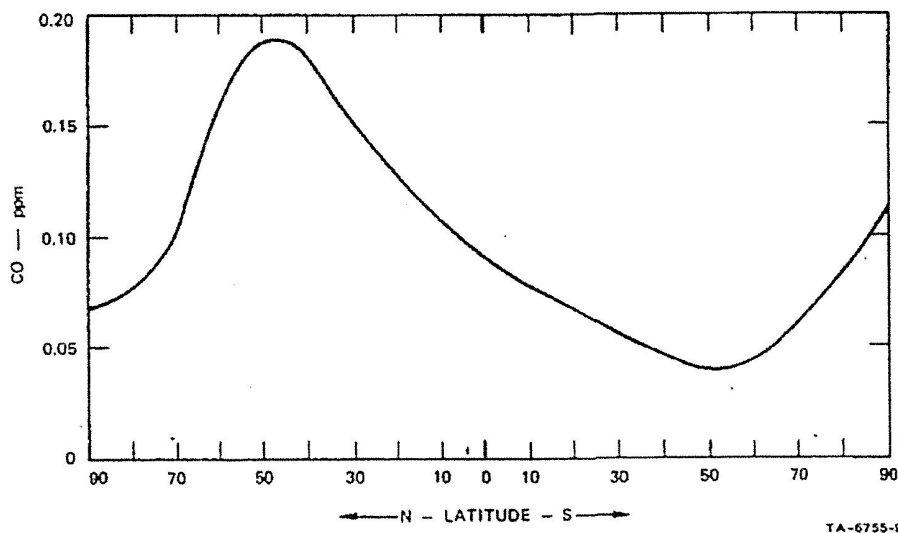
FIGURE 11   AVERAGE LATITUDE DISTRIBUTION OF CARBON MONOXIDE
IN THE PACIFIC AREA. Based on Stanford Research Institute
data from USNS Eltanin and USNS Perseus voyages 1967–1968.

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·highest concentrations, about 0.2 ppm, are found between 30° and 50°N. Southward from 30°N, CO concentrations decrease to 0.09 ppm at the equator and then to about 0.04 at about 50°S. Then southward CO concentrations apparently increase to about 0.08 over Antarctica.

If the curve in Figure 11 is considered representative of general tropospheric CO concentrations, average hemispheric CO concentrations can be estimated. Integrating this average curve and correcting for the latitudinal change in atmospheric volume gives an average CO concentration in the northern hemisphere of 0.14 ppm, 0.06 ppm in the southern hemisphere, and a global average of 0.1 ppm.

Recent data on CO background levels in Europe have been reported by Junge (1968), who was using an instrument of the SRI design. He indicates on the basis of preliminary data that during the influx of strong westerly winds over West Germany the CO concentration was never observed to drop below 0.14 ppm. In addition, some exploratory aircraft measurements in the upper troposphere over the European Arctic gave similar concentrations. Junge interprets these results as indicating a CO background level in the range of 0.1 to 0.2 ppm. These data are generally similar to the CO levels found in Greenland by SRI in the summer of 1967 and to the Pacific data in latitudes of about 50°N.

Although our knowledge of ambient CO concentrations is still incomplete, our estimate of a global average concentration of 0.10 ppm, as indicated by the average Pacific data, seems reasonable. Using this average ambient CO concentration and an estimated emission rate permits calculation of the rate at which CO is removed from the atmosphere. At a CO concentration of 0.10 ppm, the mass of CO in the atmosphere is about 5.6×10^{14} g. We have estimated the annual total CO emission rate as 2.5×10^{14} g; thus, the atmosphere contains about 2.2 years' emissions.

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This is a surprisingly short time for CO which, as we shall see, has no clearly defined reaction cycle to provide a sink.

It is obvious that a number of assumptions have gone into this estimate and it will be useful to re-examine some of them to see whether this 2.2-year residence time is too short. In this calculation it will be seen that the residence time will be in error on the short side if the emission rate is too high or the average atmospheric concentration is too low. First, the average concentration estimate is most likely high, and it seems obvious that an ambient concentration may be as low as 0.05 ppm. This would halve the residence time. The other portion of the determination, the total emission of CO, is based primarily on the emissions from gasoline engines, and it seems unlikely that this estimate is especially high. In fact, it seems more likely that this estimate is low because we have not included any marine sources, in which case the calculated residence time would be overestimated. Thus it does not seem that variations in these calculations would significantly change our conclusion, namely, that a significant sink for atmospheric CO is required by the conditions presently observed in the ambient atmosphere.

A comparison of the solar spectra data from the 1950s which, as we indicated, averaged about 0.2 ppm is comparable to the mid-latitude SRI chemical data where the observations were made, and does not give us any reason to believe that any major accumulation of CO has taken place in the approximately 15 years between these observations and the recent analyses.

C. Sources of Carbon Monoxide

The pollutant sources of CO have been recognized for many years and the amounts expected to be emitted to the atmosphere can be estimated with reasonable accuracy. This has been done in Table VI.[*] On a

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[*] Reprinted from (I).

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world-wide basis the total annual CO emission from combustion sources is 285×10^6 tons or about 2.6×10^{14} grams.

The data shown in Table VI confirm the fact that automobiles are the major source of CO, accounting as they do for 68% of the total. The magnitude of this source has been estimated, using a standard CO emission value of 2.91 pounds per gallon of gasoline (Mayer, 1965). Annual world-wide gasoline production was 379×10^6 tons in 1966 (U.S. Statistical Abstracts, 1967) which, assuming no net carryover, provides a total CO emission of 193×10^6 tons.

Coal production on a global basis amounted to 3074×10^6 tons in 1966 (U.S. Statistical Abstracts, 1967). The major CO emissions from coal were assigned to power development, industrial operations, including rail and steamship uses, residential and local uses, and coke and gas plants. Tonnages for the various uses of coal were obtained for United States and Great Britain (Clean Air, 1967). In Table VI the tonnage in each class is the sum of the U.S. tonnage plus that for the rest of the world. This latter figure assumes that the relative amounts in the various classes for areas outside the United States were the same as apply in Great Britain. Using this scheme the total annual CO emissions from coal total 12×10^6 tons.

The other major fuel is vegetal, both in the form of wood, bagasse, peat, and other noncommercial fuels, and forests consumed in forest fires. On the basis of 1952 data it was estimated that the annual use of wood fuel was 1260×10^6 tons (UN, 1956) with a CO emission of 70 pounds per ton (Darley, et al., 1966) for a total annual CO emission of 44×10^6 tons. Incineration emissions are estimated at 25×10^6 tons on the basis of the incineration of 500×10^6 tons and an emission factor of 100 lbs CO/ton. The forest fire contribution can only be estimated roughly on the following

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Table VI

ESTIMATED ANNUAL CO EMISSIONS

Source	Consumption	CO Factor	CO Emission, tons
Gasoline	379×10^6 T[a]	2.91 lb/gal[b]	193×10^6
Coal[c] (total)	$3,074 \times 10^6$ T[a]		
Power	$1,219 \times 10^6$ T[a,d]	0.5 lb/T[c]	
Industry	781×10^6 T[a]	3.0 lb/T[c]	12×10^6
Residential	404×10^6 T[a]	50.0 lb/T[e]	
Coke and Gas Plants, etc.	615×10^6 T	0.11 lb/T	
Wood and Noncommercial Fuel	$1,260 \times 10^6$ T[f]	70 lb/T[g]	44.0×10^6
Incineration	500×10^6 T	100 lb/T	25.0×10^6
Forest Fires	18.0×10^6 acres[a]	70 lb/T[g]	11.0×10^6
			285×10^6 tons
			$(2.57 \times 10^{14}$ grams$)$

[a] U.S. Stat. Abs. (1967).

[b] Mayer (1965).

[c] 13,100 Btu/lb (U.S. Stat. Abs., 1967).

[d] Nat. Soc. for Clean Air (1962-63).

[e] Heller and Walters (1965).

[f] U.N. (1963).

[g] Darley et al. (1966).

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basis. First, in the United States in 1966, forest fire acreage was 4.5×10^6 acres (U.S. Stat. Abs.); we assumed this was 25% of the global forest fire areas, giving a world total of 18×10^6 acres burned annually. Second, average fuel burned per acre was assumed to be 18 tons, which is roughly 90% of the average amount of wood growing·on an acre (McElroy, 1960; UN, 1963). Third, average CO emission from bush and green wood was taken as 70 pounds per ton (Darley, et al.,·1966). This procedure results in a total CO contribution of 11.3×10^6 tons annually. This amount is clearly not a significant factor in the total annual emissions of CO, and more detailed refinements are not justified because they could hardly make a significant change in the total.

Emissions of CO from fuel oil, natural gas, and diesel are not significant.

As shown above, the total estimated annual CO emissions are 285×10^6 tons or approximately 2.6×10^{14} grams. In 1952 Bates and Witherspoon estimated CO emissions to be 210×10^6 tons annually. Of this, 130×10^6 tons were attributed to automobiles, 40×10^6 tons to coal, and 40×10^6 tons to wood combustion and forest fires. It seems reasonable that coal is less of a source now because of the increase in the proportion of coal that is being used in highly efficient power generation processes.

There is a strong imbalance in CO emissions between the northern and southern hemispheres. On the basis of gasoline consumption, 95% occurs in the northern hemisphere (UN, 1968). Data on the other sources are not readily available, but it seems quite likely that the other combustion sources also show this strong bias toward the northern hemisphere. This is doubtless reflected in the differences in atmospheric concentrations that seem to be apparent in Fig. 11.

Although natural sources, except possibly forest fires, of CO have
not received much attention in the literature to date, there is increas-
ing evidence that trace concentrations of CO in the atmosphere could be
from natural sources. Although there is no indication of CO being a sig-
nificant portion of volcanic gases, the reported data are scarce and there
are some references to the release of CO from heated basalt rock (Rankama
and Sahama, 1949). There is one report, by Wilks (1959), that CO is
given off by vegetation and, in particular, as a result of the action of
UV radiation on chlorophyl. As part of his experiment Wilks enclosed
several growing branches in plastic bags. After several days he measured
relatively high CO concentrations in the air surrounding the growing
branches, and he cited this as an indication of CO being produced by the
plant. It seems quite possible that the CO in this situation resulted
from the artificial sealing-off of the growing branches rather than from
natural processes within the plant; however, further study is certainly
justified. Some bacteria have been found that are capable of producing
CO as a result of their metabolism (Rabinowitch, 1945).

More important evidence of a natural CO source in the surface waters
of the ocean have recently resulted from separate studies by Stanford Re-
search Institute in the Pacific, and by the Naval Research Laboratory (NRL)
in the Atlantic.

Apparently the first indication of a significant natural marine CO
source resulted from the study of atmospheric measurements made in the
Pacific in the fall of 1967 (Robinson and Robbins, 1968). These measure-
ments, which were made during an oceanographic cruise from San Francisco
to New Zealand, showed that CO concentrations had considerable diurnal
variation. The only logical explanation for short period changes in CO
in the middle of the Pacific seems to be some action of the ocean either
as a source or sink. The fact that CO concentrations in the southern

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hemisphere, as found in this trip, seem to be one-half to one-third those in the mid-latitudes of the northern hemisphere may indicate the importance of oceanic contributions in the southern hemisphere (Robinson and Robbins, 1968).

In the summer of 1968, round trip crossings were made of both the Pacific and the Atlantic with continuous measurements of CO during the four traverses. The Atlantic data are strongly affected by CO from both North America and Europe and it is hard to show any role of the ocean on the basis of the SRI air samples. The Pacific data are more readily evaluated and again seem to indicate, but not prove, that the ocean could be a CO source. A weak diurnal cycle is indicated by the data, with lower concentrations occurring in early afternoon and higher concentrations at night. A seasonal change is also possible with August concentrations being higher than early June measurements.

More recently, J. W. Swinnerton and his coworkers (1968) at the Naval Research Laboratory in Washington, D.C. made comparative CO measurements in both the atmosphere and the ocean in the Caribbean area. A review of their measurements shows that the surface water in the open ocean was supersaturated relative to atmospheric CO concentrations. On a quantitative basis this supersaturation was as much as 90 times in one area and, in general, the ocean CO concentration was at least 10 times the equilibrium saturation. Atmospheric concentrations over the open ocean ranged from about 75 to 250 ppb, which is in the same range as SRI encountered in the Pacific. These NRL data can best be explained by postulating a source of CO in the surface ocean water.

Although the source of this CO in the ocean has not been identified, a logical explanation is that it is a biological process. The siphonophores may play a major role. For example, E. G. Barham (1963) reports that siphonophores are consistently present in the deep-scattering layer

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of the ocean, and that sound is scattered where siphonophores are present in great abundance. Pickwell (1967) investigated siphonophores and found that they repetitively expel bubbles containing nearly 80% carbon monoxide. This deep-scattering layer is known to have a diurnal cycle; it is at the surface at night and descends to depths of 300 to 400 meters in the day-time. Pickwell calculated a possible normal and a maximum CO contribution to the atmosphere. The maximum contribution is 2 cc of CO per square meter of sea surface per day, with a more normal contribution of 0.02 cc of CO per square meter of sea surface per day. This source of CO would emit 362×10^6 tons per year maximum, to 3.62×10^6 tons per year minimum. The maximum contribution figure is based on unusually dense swarms of siphonophores observed only once with the maximum observed rate of bubble production. The minimum figure is probably a more normal figure and is based on typical numbers of siphonophores seen or captured. All produc-tion rates calculated by Pickwell assume no biochemical mechanism for removal of siphonophore-produced CO. The diurnal cycle of the siphono-phores bears an interesting correlation to the marine CO diurnal cycle observed by SRI on the Eltanin cruise from San Francisco to New Zealand.

Another potential natural source of CO over land areas, proposed by Went (1966), is CO produced by photoreactions of terpenes in the atmos-phere. Went estimates that 10^9 tons of volatile organics of plant origin are molecularly dispersed throughout the world each year. Photochemical oxidation of these plant volatiles by ozone or nitrogen oxide could pro-duce 61×10^6 tons of CO annually. This calculation is based on the as-sumptions that one molecule of CO will be produced per three molecules of organics (Leighton, 1961), and that the average organic molecular weight is 150. This source of atmospheric CO could contribute approxi-mately one-third of the worldwide tonnage of CO from combustion of gaso-line.

A basic question that now needs to be answered is whether the background CO in clean atmospheres originates from combustion or if biochemical utilization of CO_2 or carbonates produces CO. The diurnal changes in CO concentration found by SRI in marine air of both the northern and southern hemispheres and the air/water saturation ratios found by NRL could indicate that the ocean, or biological processes within the ocean, could be a source of CO. Data on remote land areas are not available, and thus no direct calculation can be made of the participation of land plants in a natural CO cycle.

One other presently unexplained link between CO and the biosphere exists in the case of Nereocyctis, the familiar kelp or seaweed with large floats or bladders. The floats of this kelp have been found to contain CO at concentrations of up to 800 ppm. This is obviously much higher than exists in the atmosphere and probably also in the ocean. The question as to how this occurs, whether it is just the unused residue from material absorbed from the water or whether it was produced by processes within the plant, has not been resolved.

Our current estimates of CO emissions from both urban and natural sources are summarized in Table VII. The total emission is about 350×10^8 tons/year, considering a low value for oceanic emissions. Of this total, 75×10^8 tons should be attributed to natural sources, including forest fires; and the remainder or 79% is attributed to pollutant sources. The authors believe that this value underrepresents the magnitude of the marine source, considering the large differences in air and water concentrations found by Swinnerton (1968).

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Table VII

ESTIMATED EMISSIONS OF CO FROM
URBAN AND NATURAL SOURCES

Source		Annual Emission (tons/year)
Gasoline		193×10^6
Coal		12×10^6
Noncommercial fuel		44×10^6
Incineration		25×10^6
Forest fires		11×10^6
Marine siphonophores	Max	360×10^6
	"normal"	4×10^6
Terpene reactions		60×10^6
Total		349×10^6
to		705×10^6 max

D. Scavenging Processes for Atmospheric Carbon Monoxide

Carbon monoxide at the present time is an important air pollution enigma because, in spite of its ubiquitous presence in combustion gases, we cannot enumerate any known scavenging mechanisms. That there must be one or more fairly effective processes by which CO is removed from the atmosphere is shown by the fact that, as we have mentioned, the present emission rate would double present atmospheric concentrations in about three years. There is no evidence for any general increase of atmospheric CO concentrations, and thus we must conclude that yet-to-be-discovered scavenging processes exist in our environment.

Several possible scavenging mechanisms can be postulated—gaseous reactions, absorption processes, and biological processes. These various possible processes will be evaluated briefly in the following sections.

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1. Gaseous Reactions

Bates and Witherspoon (1952) reviewed various likely gaseous reactions whereby CO might be oxidized to CO_2. The reaction with molecular oxygen

$$2CO + O_2 \rightarrow 2CO_2$$
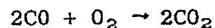
is possible, but apparently it is unimportant in the atmosphere. In this regard, Mellor (1924) records an experiment in which CO and O_2 mixtures remain unchanged after 7 years exposure to sunlight. The possibilities of CO reactions with atomic oxygen have been reviewed by Leighton (1961) and he concludes that they are unimportant. Bates and Witherspoon (1952) came to a similar conclusion. Ozone will oxidize CO to CO_2, but according to Leighton (1961), this reaction is extremely slow at atmospheric temperatures and concentrations. A high activation energy of about 20 kcal for the CO oxidation by O_3 was found by Zatsiorskii et al. (1940). Oxidation by NO_2 in the reaction

$$NO_2 + CO \rightarrow CO_2 + NO$$
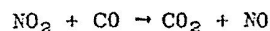
has an even higher activation energy of about 28 kcal (Brown and Crist, 1947), which essentially rules out this process.

There has also been some consideration given to the possibility that some very fast reactions occur between CO and certain intermediates of photochemical smog reactions. One possible intermediate is the hydroxyl radical. These can be produced, for example, by the photolysis of aldehydes to produce perhydroxyl, which can then be reduced to the hydroxyl radical. According to the studies of Greiner (1967) hydroxyl is a very rapid reactant with CO and there is some indication that perhydroxyl also reacts with CO. These reactions are chain-type, beginning with CO and hydroxyl and resulting in the production of CO_2 and the reformation of hydroxyl. Doyle (1968) calculates that a global average hydroxyl concentration of 10^{-9} to 10^{-8} ppm would be sufficient to convert all emitted CO to CO_2. The significance of this hydroxyl sink mechanism remains to

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be proven. A possibly serious limitation to this mechanism is the potential effect of methane (Ch_4), which can also be oxidized by hydroxyl. Since, throughout most of the troposphere, CH_4 is an order of magnitude higher in concentration than CO, 1.5 ppm versus 0.1 ppm, the major reaction for available hydroxyl may be primarily with CH_4. Only detailed and careful research will provide an answer.

Although future research with hydroxyl class radicals may be rewarding, at present we must conclude that there are no proven significant gaseous oxidation reactions for CO in the ambient atmosphere.

2. Absorption Processes

Absorption of CO on surfaces exposed to the atmosphere does not represent a sink unless some reaction can be postulated that would promote the oxidation of CO on the surface. No such reaction has been discovered.

Oceans are a recognized sink for atmospheric CO_2, and it is natural to ask whether they are also a sink for CO. Although CO solubility in seawater is about 20 ml per liter (Douglas, 1967), at present there is no reason to believe that the oceans are a CO sink because there is no recognized process or reaction that would remove CO from solution. This is in contrast to the various physical and biological processes that CO_2 can undergo. The solubility of CO is not sufficient without some reaction, because if the concentration of CO in the ocean follows Henry's law and is proportional to the partial pressure of CO in the atmosphere, a typical remote area, ambient concentration of 0.10 ppm results in a possible total of only 3.4×10^{12} g of CO in solution in the oceans of the world (volume = 1.37×10^{21} liters) even assuming uniform mixing. This is only about 2% of the estimated yearly production of CO. This clearly eliminates the ocean as a CO sink unless there are reactions occurring to remove CO from solution. An apparent diurnal cycle for CO concentrations

over ocean areas has been reported by Robinson and Robbins (1968). This seems to indicate some participation of the ocean in the CO cycle. The high CO concentrations, up to 93%, in some marine plants (Douglas, 1967) also indicate some complex, probably biological, system involving CO in the ocean. Because of low CO solubility and no available reaction mechanism, rain washout cannot be a significant CO removal mechanism.

3. Biological Processes

Even though no sink mechanism for atmospheric CO has been identified in atmospheric and surface reactions or absorption, the present atmospheric concentrations and the total emissions clearly indicate that some mechanism is removing large quantities of CO from the atmosphere. One other possible sink mechanism for atmospheric gases such as CO is in both the terrestrial and the marine biospheres.

At least two types of CO scavenging processes can be postulated for the terrestrial and marine biological populations. One is related to the presence in significant numbers of specific species of plants or animals that could metabolize CO. A second mechanism is a biochemical one in which CO would be bound to widely distributed organic compounds in much the same way it is bound by hemoglobin in blood.

One obvious biological sink of the metabolizing type could be bacteria promoted reactions that use CO as a source of carbon, e.g., Bacillus oligo-carbophilus (Rabinowitch, 1945). Jaffe (1968) has summarized other possible scavenging mechanisms involving microorganisms, including some of the methane-producing soil bacteria. No estimate can be made at this time as to the distribution of bacteria of this type either on land or in the oceans, and therefore the practicality of regarding them as a significant CO sink is unknown. However, the possibility should be recognized.

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A potential biochemical scavenging process for CO is the binding of CO to the porphyrin type compounds that are universally distributed in living materials. In particular, the heme compounds, which contain cross-linked iron, could conceivably bind CO, at least on a temporary basis and at a rate that is a function of atmospheric concentration. Since prophyrin compounds are so widely distributed, this type of process could perhaps have great potential for scavenging CO. Permanent removal from the environment would depend on whether CO subsequently reacted to form CO_2 when the porphyrin compound is broken down. Plant systems could provide a site for such reactions.

Within the biosphere, the process of plant respiration seems to provide more potential for CO pickup than does the action of bacteria, because it is known that plants are effective scavengers for a wide variety of atmospheric material, including CO_2, SO_2, O_3, H_2S, and fluorides.

A number of effects have been noted in plants after exposure to various concentrations of CO. One specific reaction is that between CO and cytochrome-oxidase. A number of different effects resulting from CO exposures are mentioned by Ducet and Rosenberg (1962), but the most frequent effect due to CO seems to be the inhibiting of plant respiration processes. Burris (1966) describes the inhibiting effect that CO has on nitrogen fixation. Exposure to relatively high concentrations, i.e., 0.01 to 1.0%, has been reported by Carr (1961) to cause a variety of visible effects.

With these various effects of CO on plants having been noted, it is perhaps logical to conclude that CO entering the plant during respiration can participate in reactions within the plant. Perhaps retention by porphyrin compounds would form one step in this process. These plant processes would provide a means for the removal of CO from the atmosphere.

If CO were absorbed by plants during the respiration cycle proportionally to the plant's use of CO_2, then a likely rate of CO absorption can be estimated. For example, by various means investigators have estimated that the atmospheric residence time for CO_2 is about four years (Junge, 1963). We also know that the concentration of CO_2 in the atmosphere is approximately 300 ppm, which provides a total mass of CO_2 in the atmosphere of 2.4×10^{18} g. If CO_2 production and absorption can be assumed to be generally in balance and if the major mechanism for removal of CO_2 is through the terrestrial and marine biosphere, the annual CO_2 exchange between the atmosphere and the biosphere will be 25% of 2.4×10^{18} g, or 6×10^{17} g. The concentration ratio of CO_2 to CO in the atmosphere is now about 300/0.10 or 3×10^3. Thus, if we assume that CO is absorbed in the biosphere in proportion to the rate of CO_2 absorption, the CO absorption rate is 2×10^{14} g annually. It is interesting that this is approximately equal to our estimate of current annual CO emissions, 2.5×10^{14} g. We might conclude from this that given no change in our present rate of emission the atmospheric CO concentration would remain more or less stable. However, in this postulated cycle the oceans play a major role and we do not have any evidence that the biological processes in the biosphere are scavenging processes. In fact, the only evidence we have to date indicates just the opposite, that the oceans are a source of CO from some as yet unknown natural processes.

At present there is no published evidence of a biological scavenging mechanism. We can only speculate that, since CO does enter the stomata during the plant's respiration cycle and since CO in high concentrations does cause some observable effects, it would seem to be logical to assume that CO in lower concentrations is also picked up from the respired air. The possibility that CO is produced rather than scavenged by vegetation must also be recognized and, as with the marine system, the only evidence

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to date indicates that CO is produced by vegetation. This is based on the fact that a limited number of tests by Wilks (1959) seemed to show CO production when he completely enclosed some growing branches for several days.

4. Summary of Scavenging Processes

In the above discussion we have described only tropospheric reactions and have ignored the photochemical reactions in which CO can participate in the high stratosphere or mesosphere. If these processes were an important CO sink, the atmospheric residence time for CO would have to be 50 to 100 years because of the slow vertical transport. We know now that the residence time of CO is about three years and thus the active scavenging mechanisms must be present at the earth's surface or within the troposphere.

Of the various scavenging processes presented in this discussion, none has been proven to be the major process responsible for the scavenging of CO from the atmosphere. However, considerable research is being done on this question and more definitive analyses can be expected in the near future.

V EMISSIONS OF SULFUR COMPOUNDS

Our previous discussion of atmospheric sulfur compounds (I) was based
on a single estimate of the total global SO_2 emissions without any consider-
ation of the details of the sources. For the mid-1960s the estimated
total SO_2 pollutant emissions were 146×10^6 tons. Of this, 70% resulted
from coal combustion, 20% from petroleum combustion and refining, and the
remainder from nonferrous smelting. In this present discussion we will
examine the estimated SO_2 emissions in more detail with regard to hemis-
pheric emission patterns. We will also present some estimates of past
changes in SO_2 emissions and some estimates for the period to the year
2000.

A. Hemispheric Sulfur Dioxide Emissions

Table VIII shows the total SO_2 emissions as estimated previously (I)
divided according to sources into northern and southern hemispheres. On
a total basis, 93% of the SO_2 emitted by pollutant sources is emitted in
the northern hemisphere. The total is estimated at 136×10^6 tons from
northern hemispheric sources out of a total 146×10^6 tons.

Table IX shows our estimate of the total hemispheric emissions of
sulfur in its various emission forms--SO_2, H_2S, and sulfate. In this
estimate H_2S emissions have been prorated over the warmer land and ocean,
those areas between 0 and $65°$ in both hemispheres, while sea spray sul-
fates have been prorated according to total ocean areas. This tabulation
shows that the atmosphere of the northern hemisphere receives over twice
as much sulfur as does the southern hemisphere. The ratio is 149×10^6
tons or 69% of the global total in the northern hemisphere compared with
66×10^6 tons or 31% in the southern hemisphere.

Table VIII

HEMISPHERIC SO_2 POLLUTANT EMISSIONS
(10^6 tons)

Source	Total SO_2	No. Hemisphere	So. Hemisphere
Coal[a]	102	98 (96%)	4 (4%)
Petroleum[a] Comb. & Refin.	28.5	27.1 (95%)	1.4 (5%)
Smelting[b]			
Copper	12.9	8.6 (67%)	4.3 (33%)
Lead	1.5	1.2 (80%)	.3 (20%)
Zinc	1.3	1.2 (90%)	.1 (10%)
Total	146	136 (93%)	10 (7%)

[a] United Nations Statistical Papers – World Energy Supplies 1963–1966, Series J, No. 11 Tables 2 and 9.

[b] U.S. Bureau of Mines, Mineral Trade Notes Vol. 64, No. 9 and 12 (1967).

Table IX

TOTAL HEMISPHERIC SULFUR EMISSIONS
(10^6 tons S)

Source	Total	No. Hemisphere	So. Hemisphere
Pollutant SO_2 Sources	73	68	5
Biological H_2S (Land)	68	49[a]	19[a]
Biological H_2S (Marine)	30	13[b]	17[b]
Sea spray	44	19[c]	25[c]
Total	215	149 (69%)	66 (31%)

[a] Based on ratio of land area between 0 and 65° N and S.

[b] Based on ratio of ocean areas between 0 and 65° N and S.

[c] Based on ratio of ocean areas in both hemispheres.

The hemispheric imbalance in SO_2 emissions points up the opportunity that exists to check the effects, if any, that SO_2 pollutant emissions may exert on atmospheric parameters. Parallel experiments in the northern and southern hemispheres should provide a situation where most factors except pollutant backgrounds could be generally equated and thus the impact of the pollutants on the atmosphere could be evaluated.

B. <u>Past and Future Sulfur Dioxide Emissions</u>

Sulfur dioxide has been a major pollutant throughout the history of industrial processes, at least since the first smelting of copper sulfide ore and the beginning of the widespread burning of soft coal.

On the basis of available fuel and smelting data, we have estimated the SO_2 pollutant emissions for the period 1860-1965. These are shown in Table X. Figure 12 shows the total SO_2 estimate as a function of time over this 100-year period. In making this estimate, the SO_2 emission factors used in our previous study (I) were used for calculating all the data for the past. For the emissions from petroleum combustion the factor includes SO_2 released both in refining and in combustion, expressed as a function of total consumption.

Figure 12 clearly shows that there has been a major increase of about 65×10^6 tons in SO_2 emissions between 1950 and 1965. As shown in Table X, 36×10^6 tons or 55% of this increase is related to increased coal combustion and 20×10^6 tons or 31% is due to increased petroleum usage. The effects of the depression in the 1930s and World War II in the 1940s are evident in these data, although the 10-year spacing of data points does not emphasize these factors. The lack of readily available production data for lead and zinc before 1900 is not a serious factor in judging the trend in SO_2 emissions, because of the small contribution from these sources.

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Table X

ESTIMATED HISTORICAL SO_2 EMISSIONS[*]
(10^6 tons)

	Coal	Petroleum	Copper	Lead	Zinc	Total
1860	5.0	0.0	0.22			5.22
1870	7.8	0.01	0.24			8.05
1880	12.2	0.07	0.26			12.53
1890	18.7	0.17	0.68			19.55
1900	28.1	0.33	1.60	0.47	0.15	30.65
1910	42.1	0.70	2.84	0.61	0.26	46.51
1920	49.5	1.79	3.26	0.54	0.22	55.31
1930	51.3	3.12	3.52	0.93	0.46	59.33
1940	61.0	4.62	5.46	0.97	0.53	72.58
1950	66.0	8.30	5.92	0.86	0.60	81.68
1960	95.7	19.9	10.0	1.28	1.0	127.88
1965	102.0	28.5	12.9	1.5	1.3	146.20

[*] Based on the following production data references:

Coal: Peaceful Uses of Nuclear Energy, UN, 1956, Table XXIII.

Petroleum: Peaceful Uses of Nuclear Energy, UN, 1956, Table XXIII.

Copper: McMahon, A. D., Copper--a materials survey, U.S. Bureau of Mines I.C. 8225 (1965), Table 26; and Herfindahl, O. C., Copper Costs and Prices: 1870-1957, John Hopkins Press, 1959, Tables 2 and A-1.

Lead: U.S. Bureau of Mines, Materials Survey: Lead (1951); and U.N. International Lead and Zinc Study Group, Factors Affecting Consumption, Appendix 1 (1966).

Zinc: U.S. Bureau of Mines, Materials Survey: Zinc (1951); and U.N. International Lead and Zinc Study Group, Factors Affecting Consumption, Appendix 1 (1966).
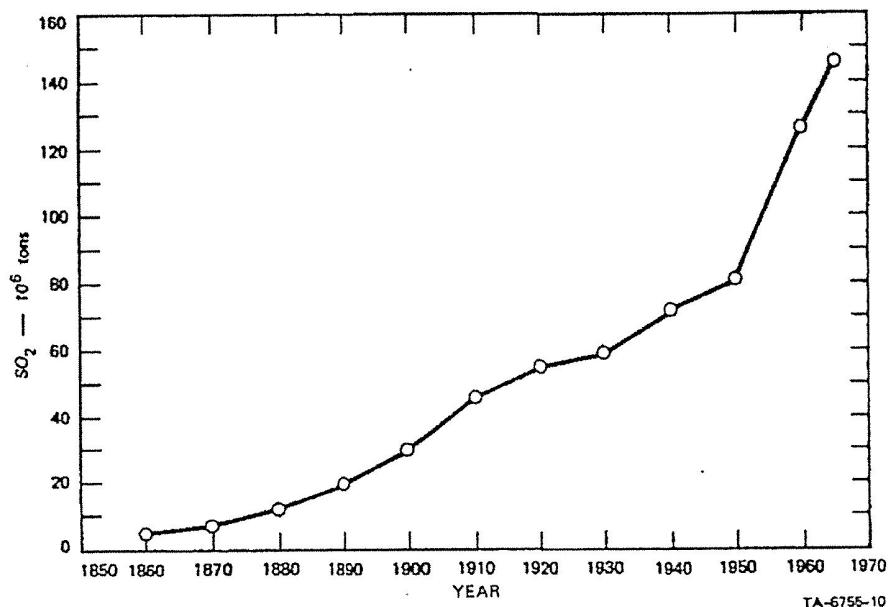
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FIGURE 12   ESTIMATED HISTORICAL SO$_2$ EMISSIONS

In the 25 years between 1940 and 1965, SO$_2$ emissions have essentially
doubled. Before 1940 it had taken 35 years, since 1905, for SO$_2$ emissions
to double. Other estimates have been made of global SO$_2$ emissions; Katz
(1956) for example estimated 1940 SO$_2$ emissions at 78 x 10^6 tons as com-
pared with our 72 x 10^6 tons. Such agreement within 10% is certainly
satisfactory when the approximations entering into these estimates are
considered.

The emissions of SO$_2$ have changed rapidly in the past 10 years and
further increases can be expected, although limits on sulfur content in
fuels may be significant factors in any future projections. Table XI
presents our estimate of global SO$_2$ emissions for the period to 2000 if
no allowances are made for the introduction of additional emission con-
trols. Figure 13 shows the total estimated global SO$_2$ emissions for the
period 1940 to 2000.

Table XI

PROJECTED SO$_2$ EMISSIONS 1965-2000
BASED ON 1965 EMISSION FACTORS
(10^6 tons per year)

|		1965	1970	1980	1990	2000
Coal						
Production increase	0.2% yr^{-1}					
SO$_2$ increase	0.2% yr^{-1}	102	103	105	107	109
Petroleum						
Production increase	6.2% yr^{-1}					
SO$_2$ increase	6.2%	29	38	62	100	162
Smelting copper						
Production increase	4.3% yr^{-1}					
SO$_2$ increase	4.3%	13	16	23	33	47
Lead						
Production increase	6.3% yr^{-1}					
SO$_2$ increase	6.3%	1.5	2.0	3.3	5.4	8.8
Zinc						
Production increase	6.1% yr^{-1}					
SO$_2$ increase	6.1%	1.3	1.7	2.7	4.3	6.9
Total SO$_2$ (1965 control rate)		147	161	196	250	333
Percent relative to 1965		100%	109%	133%	170%	226%

56
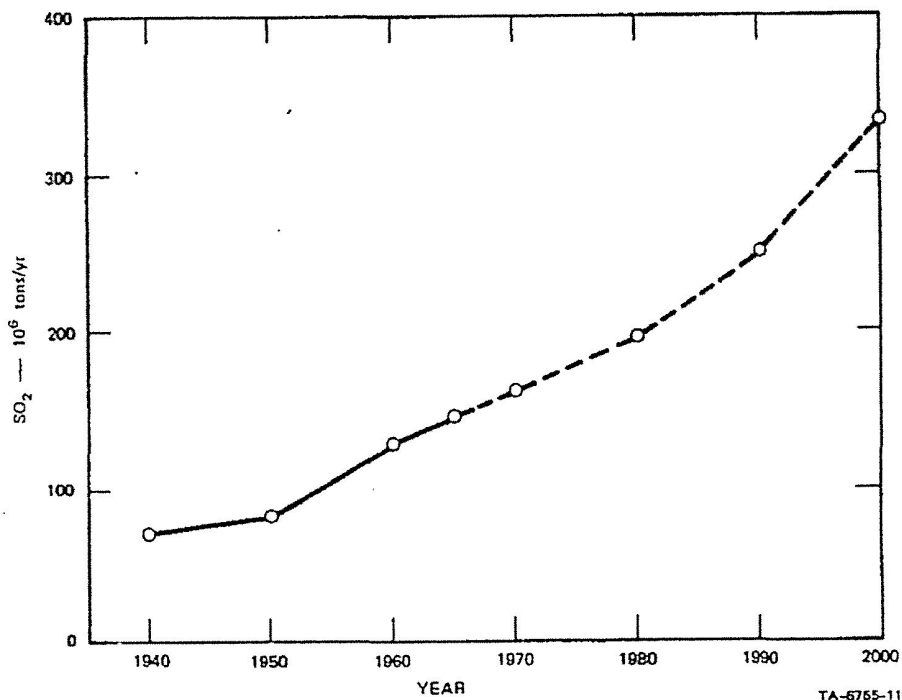
FIGURE 13   PROJECTED GLOBAL SO₂ EMISSIONS BASED ON 1965
EMISSION FACTORS

As indicated in Table XI, coal consumption is expected to increase
least over the period, at a rate of 0.2% per year (SRI, 1969). The rest
of the possible SO_2 sources are expected to increase at appreciably faster
rates, petroleum at 6.2% per year (SRI, 1969), copper smelting at 4.3%
per year (UN, 1966), lead smelting at 6.3% per year (UN, 1966), and zinc
smelting at 6.1% per year (UN, 1966). If SO_2 emissions also increase at
these same rates, by the year 2000, estimated SO_2 emissions would be
333×10^6 tons annually. In this projection it will be after 1990 before
coal ceases to be the largest single source of SO_2.

These projected emissions can also be related to our estimate of
natural emissions. Table IX indicates that natural sources annually ac-
count for about 142×10^6 tons of sulfur on a global basis and about

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81×10^6 tons in the northern hemisphere. According to our SO_2 emission projections in Table XI and Figure 13, global pollutant emissions will begin to exceed natural sources of sulfur about 1995. In the northern hemisphere, if 90% of the SO_2 is attributed to northern hemispheric sources, pollutant sources of sulfur will exceed the natural sources about 1975. New control measures on major sulfur emissions can be expected to affect these estimates, however.

VI NITROGEN COMPOUNDS

The cycle of nitrogen compounds through the environment is complex because there are at least four gaseous compounds and two solid nitrogenous compounds. These materials--N_2O, NO, NO_2, NH_3, ammonium compounds, and nitrates--are for the most part interrelated and the environmental cycle is complex.

The major pollutant emissions in the nitrogen group are NO and NO_2. These are usually not differentiated and are expressed as NO_2 or NO_x. The annual global pollutant emissions were estimated to be 50×10^6 tons as NO_2 (I).

In this supplemental study we have taken another look at the nitrogen cycle and believe that certain changes are warranted in estimates of those portions of the cycle involving the natural emissions of NO and NO_2 and the formation of nitrate aerosols.

A. Atmospheric Concentrations of Nitric Oxide and Nitrogen Dioxide

We previously estimated that the average background concentration of NO_2 was about 1 ppb. Essentially, this estimate was based on data from four sources--Panama (Lodge and Pate, 1966); Florida and Hawaii (Junge, 1956); the mid-Pacific (Lodge, et al., 1960); and Ireland (O'Connor, 1962). To these data should be added data from the North Carolina Appalachians (Ripperton, et al., 1968), and from Pike's Peak, Colorado (Hamilton, et al., 1968). Some data are also available for the Antarctic (Fischer, et al., 1968). The results of these various sampling studies are summarized in Table XII.

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Table XII

SUMMARY OF NITROGEN OXIDE CONCENTRATIONS

Location	Results		Reference
Panama			Lodge and Pate, 1966
(Marine)	NO_2:	0.5-5 ppb	
(Forest)	NO_2:	0.5-4 ppb	
	NO:	0 -6 ppb	
Mid-Pacific	NO_2:	94% of samples < 1 ppb	Lodge, et al., 1960
Florida	NO_2:	0.9 ppb	Junge, 1956
Hawaii	NO_2:	1.3 ppb	Junge, 1956
Ireland	NO_2:	0.34 ppb (Spring)	O'Connor, 1962
	NO_2:	0.2 ppb (Fall)	
North Carolina	NO_2:	4.0 ppb	Ripperton, et al., 1968
	NO:	2.6 ppb	
Pike's Peak	NO_2:	4.1 ppb	Hamilton, et al., 1968
	NO:	2.7 ppb	
Antarctic	NO_2:	Avg < 0.6 ppb	Fischer, et al., 1968

On the basis of these data we have assumed the following mean conditions for our atmospheric cycle estimates for nitrogen compounds:

Land areas between 65°N and 65°S: NO = 2 ppb
                                                   NO_2 = 4 ppb

Land areas north and south of 65° and   NO = 0.2 ppb
all ocean areas: NO_2 = 0.5 ppb

Applying these values to the various global sectors results in an estimated total atmospheric mass for NO of 4.7×10^6 tons (4.2×10^{12} g) and for NO_2, 13×10^6 tons (11.8×10^{12} g). On a nitrogen basis the totals are 2.2×10^6 tons (2×10^{12} g) of NO-N and 4.0×10^6 tons (3.6×10^{12} g) of NO_2-N.

B.   The Environmental Nitrogen Cycle

We have reanalyzed the cycle of nitrogen and nitrogen compounds through the atmospheric environment. The revised estimate of the annual nitrogen cycle is shown in Figure 14 in terms of total nitrogen in the various fractions of the cycle. The cycle expressed in terms of nitrogen component tonnages is shown in Figure 15. The cycle for nitrogen is made up essentially of three separate cycles--the N_2O cycle, the NH_3 cycle, and the NO_x cycle. There is a major difference between the estimated cycle and our previous one (I) in that we have not found it necessary to include an association between NO_x and NH_3 phases of the cycle. In the following discussion, we will describe the revised estimate, which is based on the circulation of nitrogen as shown in Figure 14.

1.   The Nitrous Oxide Cycle

The understanding of N_2O in our environment has improved in recent years. Now the measurements of the ambient concentration seem to be fairly consistent and indicate a level of about 0.25 ppm (Bates and Hays, 1967: Junge, 1968). Measurements have also shown that there is N_2O present in the ocean and that some mechanism in the ocean is providing
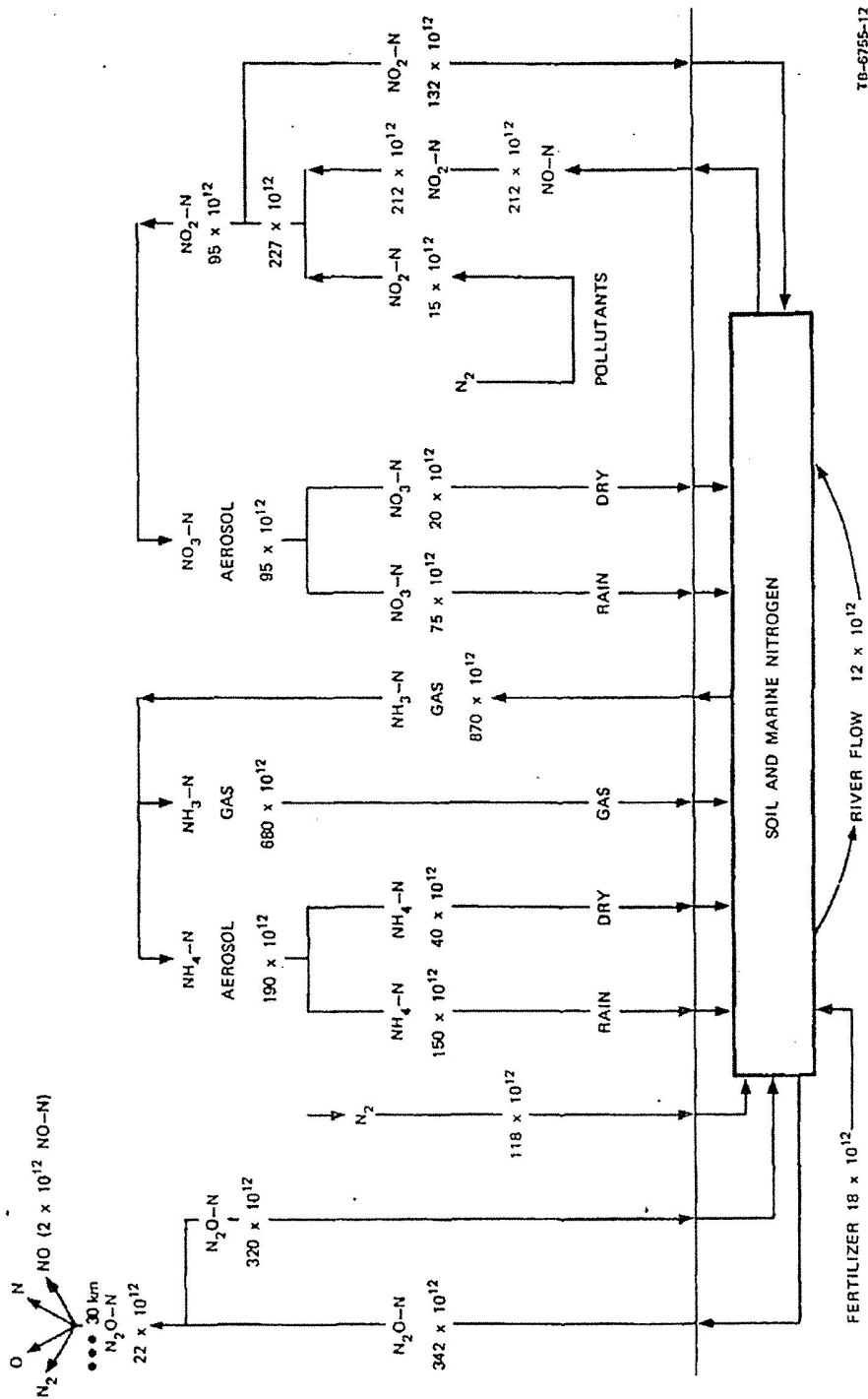
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FIGURE 14   ENVIRONMENTAL NITROGEN CIRCULATION IN TERMS OF NITROGEN QUANTITIES PRESENT IN NITROGEN COMPOUNDS, GRAMS PER YEAR
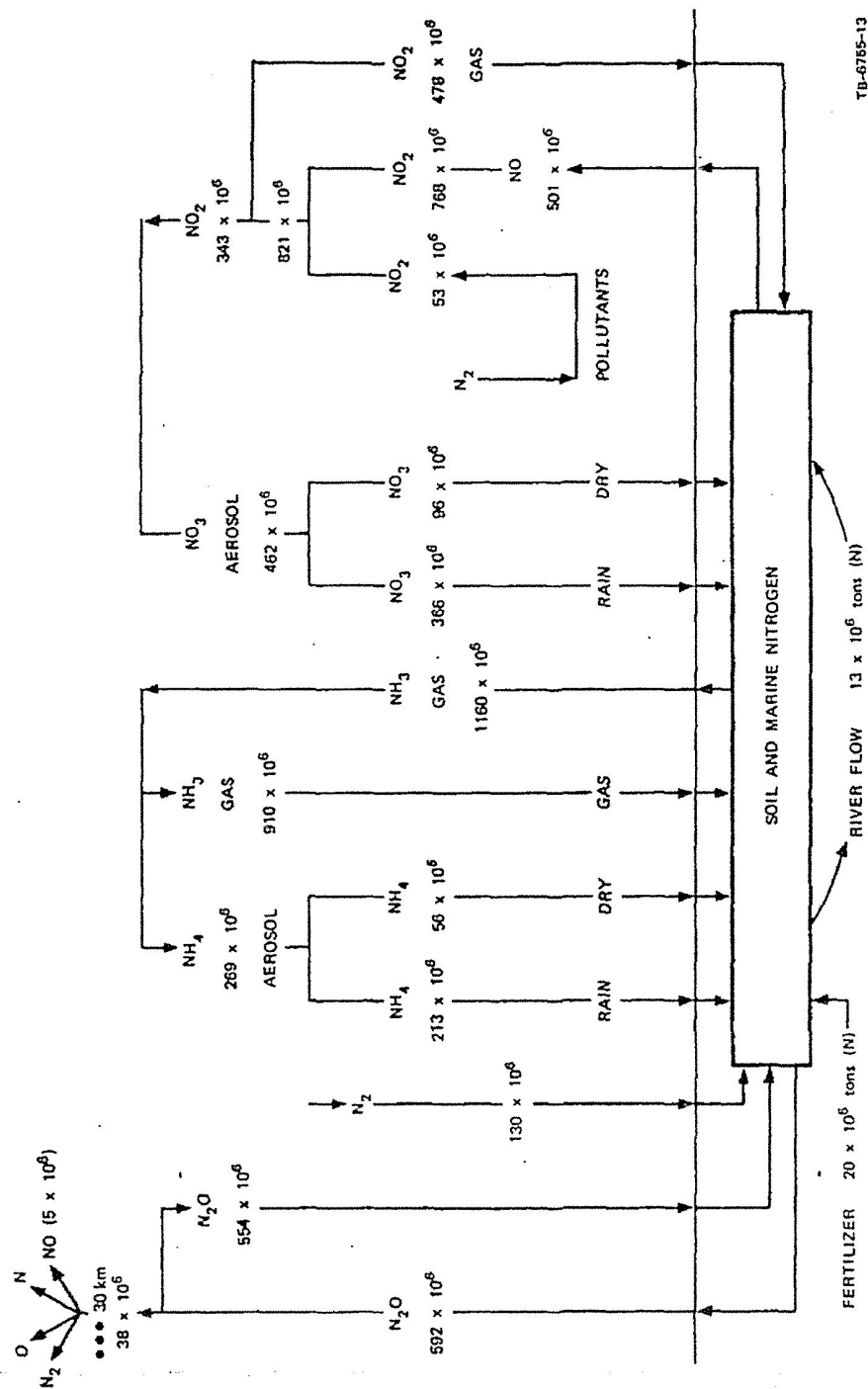
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FIGURE 15   ENVIRONMENTAL CIRCULATION OF NITROGEN COMPOUNDS, TONS PER YEAR

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a minor sink (Craig and Gordon, 1963). These facts are supplemented by
newer calculations of the annual stratospheric photodissociation rate
indicating a much lower value, 24×10^{12} g N_2O-N (Bates and Hays, 1967)
compared with the previous rate estimate of about 6.3×10^{14} g/yr made
by Goody and Walshaw (1953).

This previous estimate of N_2O destruction was generally balanced by
production in the soil at a similar rate, 10^{15} g/yr as N_2O, based on the
soil production studies of Arnold (1954). Reactions in the soil have been
summarized in detail by Bates and Hays (1967), who point out the various
factors, such as moisture and pH, that affect Arnold's N_2O production
estimate. They also note, however, that N_2O is destroyed by some micro-
biological reactions, e.g., those described by Wijler and Delwiche (1954),
with the resultant production of N_2. Burris (1966) has reported that the
presence of N_2O will inhibit the fixation of N_2. Thus, for N_2O there is
both production and destruction at the soil surface.

In our estimate of the circulation of N_2O, both the stratospheric
and the soil sinks have been considered. We also suggest the possibility
that N_2O is absorbed in plant tissues during photosynthesis in a manner
similar to our argument for the vegetation sink for CO (I). In our
previous discussion we assumed absorption by vegetation in the same
proportion as the atmospheric ratio with CO_2; in the case of N_2O this
ratio is 300/0.25 or 1200 to 1. As we did previously (I), we estimate
the annual production rate of CO_2 as 6×10^{17} g on the basis of a four-
year CO_2 residence time. At this rate the proportional rate of consump-
tion of N_2O would be 5×10^{14} g/yr (500×10^6 tons/yr) or about half the
N_2O emission rate calculated by Arnold. However, his results were very

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approximate and a factor of 2 is probably not too large a difference. We thus have the following estimate for N_2O in terms of N_2O-N.

Total N_2O-N in atmosphere	1.3×10^{15} g
Total N_2O-N in oceans (Craig and Gordon, 1963)	0.25×10^{15} g
Estimated photodissociation (Bates and Hays, 1967)	2.2×10^{13} g
Estimated biosphere loss	3.2×10^{14} g
Total production (to balance)	3.4×10^{14} g

$$\text{Residence time} = \frac{1.55 \times 10^{15}}{3.4 \times 10^{14}} = 4.5 \text{ years}$$

This conclusion as to the residence time is about the same as that estimated by Junge (1963). If we used an annual CO_2 cycle of 10^{18} g, as estimated from Rabinowich (1945), we would have to postulate a greater N_2O loss to the biosphere and a shorter, 2.9 years, residence time for N_2O.

Basically, the N_2O cycle is a balanced system of biological production and a biological sink with an additional stratospheric sink that accounts for less than 10% of the total loss of N_2O.

2. Nitrogen Fixation

Nitrogen is estimated as entering the soil at a rate of 118×10^{12} g/yr. This is a bacterial fixation process and the estimated rate is based on calculations by Hutchinson (1954). This portion of the cycle does not relate to other portions except that soil nitrogen is a source of NH_3, NO_x, and N_2O.

3. The Ammonia Cycle

The ammonia and ammonium aerosols that are present in the atmosphere are due primarily to ammonia production in the soil. The sea surface has

not been clearly identified either as a source or a sink; however, data of Lodge and Pate (1966) may be interpreted as indicating an NH_3 source in the Caribbean area. The magnitude of the biospheric NH_3 source has not been measured; however, following our previous techniques we can estimate the probable emission from concentration data. It was estimated (I) that 6 ppb is a reasonable average for NH_3 in the ambient atmosphere. At this concentration, the total amount of NH_3-N in the atmosphere at any one time would be about 17×10^{12} g. Because of its high solubility, and its origin at the surface, NH_3 can probably be assumed to have a rather rapid turnover, perhaps about 1 week, or even less, similar to that of SO_2. Georgii and Weber (1960) indicate on the basis of chemical sampling and rain analysis in Frankfort, Germany, that NH_3 concentrations in the atmosphere were reduced by about 50% by rain, while the reduction in SO_2 concentrations was 36%, and NO_2 was reduced 24%. Thus the assumption of similar residence times for NH_3 and SO_2 is probably not unreasonable. If the residence time for NH_3 were about one week, this would indicate an annual production of about 50 times the atmospheric mass or 850×10^{12} g.

In Figure 14 the production of NH_3-N is set at 870×10^{12} g in order to balance the calculated scavenging mechanisms, namely, gaseous deposition and aerosol formation processes.

Gaseous deposition for NH_3 is calculated from a set of fairly simple assumptions--a deposition velocity of 1 cm/sec and a global average concentration of 6 ppb. The deposition velocity assumes that NH_3 is as reactive with vegetation, land, and water surfaces as is SO_2. This seems to be generally reasonable considering comparative data on NH_3 and SO_2 in rainwater reported by Georgii and Weber (1960). The average NH_3 concentration is an approximate median of scattered remote measurements as presented in the earlier report (I). If there were more data to draw on, it

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would be desirable to try to differentiate between land and ocean areas, because indications are that land areas are the major source of natural NH_3 production.

Aerosol deposition of ammonium compounds represents the second scavenging mechanism for atmospheric NH_3. Ammonia reactions can occur readily in cloud and fog droplets, and reactions between NH_3 and SO_2 in solution to form $(NH_4)_2SO_4$ are estimated to be a major scavenging process for SO_2. The NH_4-N mass that is estimated as being included in this phase of the cycle is 190×10^{12} g NH_4-N. This amount is 125% of the estimated amount of NH_4-N present in precipitation, if the 25% is added to account for dry aerosol deposition. The amount of NH_4-N deposited on a global basis in rain is estimated on the basis of Eriksson's (1952) tabulation of NO_3-N and NH_4-N in precipitation. These data indicate that there is a latitudinal distribution of NO_3-N and NH_4-N, with peak depositions occurring in the northern hemisphere. Figure 16 is our interpretation of the data presented by Eriksson (see Figures 4 and 5 of Eriksson, 1952). As indicated by Figure 16 the same latitude distribution is applied to both NH_4-N and NO_3-N. The total deposition rate for NH_4-N was determined from Figure 16 by multiplying the deposition rate by the global area in 10-degree-latitude belts. The zero level of deposition in the polar regions is in general agreement with measurements of polar snow, especially in the Antarctic (Wilson and House, 1965). The total NH_4-N estimated to be brought to earth by precipitation is 150×10^{12} g/yr. This is a global rate and no differentiation is made between land and ocean areas.
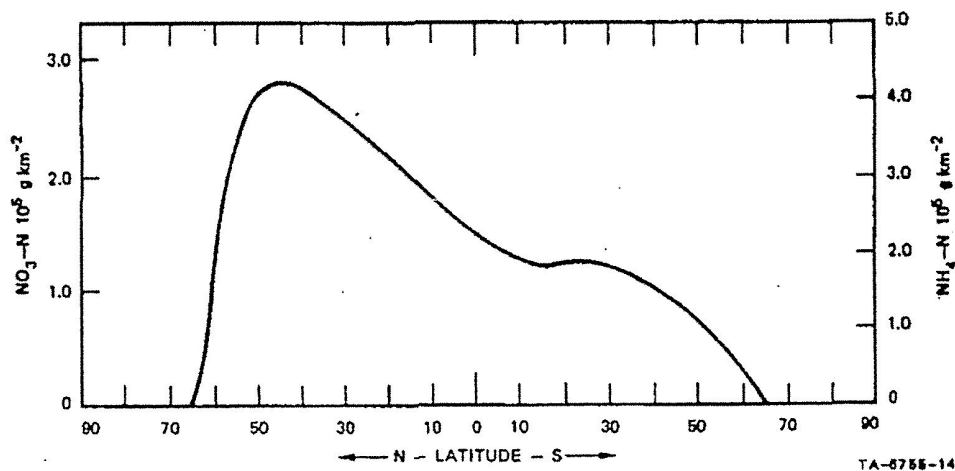
FIGURE 16 NH$_4$-N AND NO$_3$-N DEPOSITED BY PRECIPITATION ANNUALLY
AS A FUNCTION OF LATITUDE——From Eriksson, 1952, Figs. 3 and 4.

4. The Cycle of Nitric Oxide and Nitrogen Dioxide

The third major phase of the nitrogen cycle is that entailing emissions of NO and NO$_2$ and the scavenging processes for both these gases and the nitrate aerosol resulting from reactions of NO$_2$ in the atmosphere.

The most readily recognized sources of atmospheric NO$_x$ compounds are pollutant emissions. We have estimated these emissions to be ~~45~~ 14.6 x 10^{12} g/ yr NO$_2$-N. Table XIII shows the distribution of NO$_2$ pollution sources as we estimated them in our previous report (I).

As indicated by Figure ~~14~~ 15, the major natural NO$_x$ emission is estimated to be NO at a rate of ~~182 x 10^{12} g/yr.~~ 501 x10^6 tons/yr. On the basis of our previously estimated average NO concentrations, this is equivalent to an NO residence time in the atmosphere of four days. This NO is scavenged readily by oxidation in the atmosphere, probably mainly through processes including ozone (Ripperton, et al., 1967). Gaseous deposition of NO is considered to be negligible because of its low solubility and low rate of reaction with surfaces. This natural NO$_2$ and the industrial NO$_2$ are scavenged both by gaseous deposition at a rate of 132 x 10^{12} g/yr NO$_2$-N and through

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(See corr. inside front cover)

Table XIII

WORLDWIDE URBAN EMISSIONS OF NITROGEN OXIDES
(AS NO_2)

Fuel	Source Type	Fuel Usage	Emission Factor	NO_2 Emission
Coal	Power Generation	$1,219 \times 10^6$ tons[a]	20 lb/ton[d]	12.2×10^6 tons
	Industrial	$1,369 \times 10^6$ tons[a]	20 lb/ton[d]	13.7×10^6
	Domestic/Commercial	404×10^6 tons[a]	5 lb/ton[d]	1.0×10^6
Petroleum	Refinery Production	$11,317 \times 10^6$ bbl[a]	6 ton/10^5 bbl[e]	0.7×10^6 tons
	Gasoline	379×10^6 tons[a]	0.113 lb/gal[d]	7.5×10^6
	Kerosene	100×10^6 tons[a]	0.072 lb/gal[d]	1.3×10^6
	Fuel Oil	287×10^6 tons[a]	0.072 lb/gal[d]	3.6×10^6
	Residual Oil	507×10^6 tons[a]	0.104 lb/gal[d]	9.2×10^6
Natural Gas	Power Generation	2.98×10^{12} ft³[b]	390 lb/10^6 ft³[d]	0.6×10^6 tons
	Industrial	10.72×10^{12} ft³[b]	214 lb/10^6 ft³[d]	1.1×10^6
	Domestic/Commercial	6.86×10^{12} ft³[b]	116 lb/10^6 ft³[d]	0.4×10^6
Others	Incineration	500×10^6 tons[c]	2 lb/ton[d]	0.5×10^6 tons
	Wood Fuel	466×10^6 tons[c]	1.5 lb/ton[d]	0.3×10^6
	Forest Fire	324×10^6 tons[a]	5 lb/ton[f]	0.8×10^6
			Total	52.9×10^6 tons

References

a. 1967 U.S. Statistical Abstracts.

b. Figure is 1.28 x U.S. usage as per 1967 U.S. Statistical Abstracts.

c. World Forest Inventory, U.N. 1963.

d. Mayer, M., "Pollutant Emission Factors," USPHS, May 1965.

e. Elkin, H.F., In. "Air Pollution," Vol. II, A. C. Stern, Ed., Academic Press, N.Y. 1962.

f. Gerstle, R. W. and D. A. Kemnitz, J. Air Pollut. Control Assoc. 17, 324 (1967).

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oxidation to nitrate aerosol at a rate of 95×10^{12} g/yr NO_3-N. Gaseous deposition for NO_2 is based on our previously determined mean concentrations and a deposition velocity of 1 cm/sec. This deposition velocity is an approximation of experimental data obtained over alfalfa and oats by Tingey (1968). Estimation of the precipitation of NO_3-N, 75×10^{12} g/ yr, is based on Figure 16 and Eriksson's (1952) data, as was our estimate of NH_4-N deposition. Dry deposition of NO_3-N particulate material is estimated at 25% of the precipitation deposition.

5. Other Factors of the Nitrogen Cycle

The nitrogen cycle estimate is completed by our indication of the amount of fertilizer added to the soil, 18×10^{12} g/yr as N, and the N transported from land to ocean by the rivers, 12×10^{12} g/yr.

C. Discussion of the Nitrogen Cycle

This method for estimating the cycle for nitrogen is superior to the prior method (I) in that it does not require reactions of NH_3 to form nitrate to achieve a balance. This has been done mainly by reducing the amount of deposition of NH_4-N and NO_3-N needed in the circulation model. This is apparently supported by Eriksson's (1952) data. Relatively low deposition rates in the southern hemisphere of approximately 1 kg/10^4 m^2 for NO_3-N and NH_4-N are supported by data from central Australia, reported by Wetselaar and Hutton (1963). These changes in the circulation model seem to be reasonable and in line with available data. Since no satisfactory reactions are known for converting NH_3 to a nitrate compound, the fact that such a reaction is no longer needed in the calculations is a very significant development.

The recognition of a significant natural emission in the form of NO is also an important phase of this model. The total mass of the natural NO-N emission is about 80% larger than was estimated for natural NO_2-N emissions in our previous model (I).

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The weak point in the nitrogen circulation model is primarily the small amount of available data that is applicable to the task. Differential data for land and ocean areas would be especially valuable in making more realistic estimates of the masses of material that enter into various portions of the cycle.

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